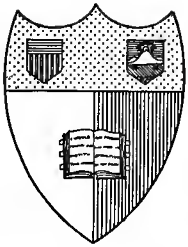

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AND OF
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FOREWORD

BY SIR CHARLES CHEERS WAKEFIELD, BART.,
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THE art of Lubrication is comparatively old, but it is only since the discovery of mineral oil that it has come to be known as a science. Having in view its importance to industry, little has been written on the subject, which is one of some complexity, demanding the threefold co-operation of Chemist, Engineer and Physicist.

Though the theory of lubrication leaves much to be understood, good progress is being made by research into the relationship between chemical constitution and friction. The Engineer also is contributing his quota in determining the best way of applying the lubricant.

The actual user of lubricating oils has been handicapped in the past through want of expert guidance and has had to draw upon his own experience or on that of his friends or rely upon the advice of the Oil Manufacturer, which, though in the main good, leaves much that is lacking. It is to meet this want that Mr. Elliott A. Evans has in this treatise laid bare the fundamental considerations in the selection of a lubricant.

Such a book, written by one whose experience in all branches of the subject is beyond question, should commend itself to a wide range of readers.

PREFACE

AFTER repeated requests from chemists, engineers, and others, for a useful non-too-technical book on lubricating oils, the author was prompted and urged by Mr. Clifford, Librarian to the Chemical Society, London, to write a book on the subject with a view to assist chemists in compiling specifications, and examining lubricating oils, also to give engineers an insight into the application and properties of such oils, and the interpretation of their specifications. The very comprehensive book, *Lubricants and Lubrication*, by Archbutt and Deeley, is too technical except for the specialist or the person who desires knowledge on a specific section of the subject. The several books on oils, such as *Chemical Technology and Analysis of Oils, Fats, and Waxes*, by Lewkowitch, and *Treatise on Petroleum*, by Redwood, cover their sphere admirably, but they do not provide that information for which the author has been repeatedly asked. Chemists require detailed information of the methods, both physical and chemical, used in the laboratory to examine the oils, and to be in a position to pass an opinion upon their relative merits ; whereas the engineer must be in a position to understand the chemist's report and to put the oil to a practical test with an appreciation of the material which he has under supervision. With these facts in mind it has been the author's endeavour to include only those tests which are commonly demanded, and a discussion of those branches of the subject which are of general interest, and to exclude anything which is controversial or highly technical.

The subject-matter has been drawn from the author's experience and close association with the science of lubrication both in the laboratory and the workshop, also from numerous technical journals, papers, and books. Wherever possible the name of the author and the source of reference is given in the text.

With the valuable assistance of Mr. Clark (draughtsman to Messrs. C. C. Wakefield and Co., Ltd.) and Messrs. A. Gallenkamp and Co., Ltd., explanatory drawings have been inserted. Throughout the writing of this book much encouragement has been given by numerous friends and by Messrs. C. C. Wakefield and Co., Ltd. To them profound thanks are offered.

In conclusion, the Author would be grateful for the notification of any errors which the reader may observe; or for suggested methods of increasing the value of future editions.

ELLIOTT A. EVANS.

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EDITORIAL NOTE

THE DIRECTLY-USEFUL TECHNICAL SERIES requires a few words by way of introduction. Technical books of the past have arranged themselves largely under two sections: the Theoretical and the Practical. Theoretical books have been written more for the training of college students than for the supply of information to men in practice, and have been greatly filled with descriptions of an academic character. Practical books have often sought the other extreme, omitting the scientific basis upon which all good practice is built, whether discernible or not. The present series is intended to occupy a midway position. The information, the investigations, and the discussions are to be of a directly useful character, but must at the same time be wedded to that proper amount of scientific explanation which alone will satisfy the inquiring mind. We shall thus appeal to all technical people throughout the land, either students or those in actual practice.

CONTENTS

PAGE

FOREWORD viii

PREFACE ix

EDITORIAL NOTE xi

CHAPTER I

HISTORY OF PETROLEUM 1

CHAPTER II

OIL REFINING . . . 5

CHAPTER III

OCCURRENCE OF FATTY OILS . . . 8

Fixed or fatty oils.

CHAPTER IV

PHYSICAL TESTS 11

Flash point—Fire point, or fire test—Specific gravity—Viscosity—Redwood viscometer—Engler viscometer—Saybolt viscometer—The expression of viscosity—Cold test—Chill point—Loss on evaporation—Demulsification value—Specific heat—Method of fusion of ice with Bunsen's ice calorimeter—Distillation test.

CHAPTER V

CHEMICAL TESTS 58

Acidity—Saponification value—Determination of fatty oil in a compound oil—Determination of a mineral oil in a compound oil—Determination of a fatty oil in a compound oil by estimating the glycerol content—Determination of a fatty oil in a compound oil by the fatty acid content—Iodine value—Bromine value.

CHAPTER VI

CHEMICAL TESTS (*continued*) 73

Sulphur determination—Moisture—Unsaturated cyclic hydrocarbons—Paraffin—Asphalt—Carbon residue test: Gray's method—Gumming test—Coke value—Artificial thickners—Transformer oil—Method of test.

CHAPTER VII

PAGE
Oxidation of Petroleum 93
Production of asphalt by the oxidation of petroleum.

CHAPTER VIII

Oleography 97

CHAPTER IX

Selection of Lubricants 102
Selection of lubricants.

CHAPTER X

Oils Employed 108

Appendix 123
Treatment of corks used in Soxhlet and other extraction apparatus.

Index 124

LIST OF ILLUSTRATIONS

PAGE
Gray's flash point apparatus 15
Pensky-Martens flash point apparatus 15
Pensky-Martens flash point apparatus 17
Ignition point apparatus 19
Specific gravity bottle 20
Hydrometer 20
Ostwald viscometer 22
Redwood viscometer 25
Viscosity temperature curve 28
Engler viscometer 31
Saybolt viscometer 33
"Cold test" apparatus 41
Solid CO_2 receiver 42
Vaporimeter 46
Air regulator 47
Toluene vapour bath 48
Bunsen calorimeter 51
Electrical resistance for specific heat 53
Distillation apparatus 56
Separating funnels 58
Saponification flask 60
Esling's apparatus 73
Bomb 75
Apparatus for moisture determination 79
Sludge test apparatus 89

LUBRICATING AND ALLIED OILS

CHAPTER I

HISTORY OF PETROLEUM

It is difficult to find a solitary individual to whom oil is not of interest and value ; in fact, it is perhaps impossible to imagine how any article could be in more universal demand than oil. The demand for oil dates back to prehistoric times, but it is only within the past decade that the oil industry has grown to its present dimensions. The future holds even greater possibilities for oil than the past has done for coal. A revolution in the oil industry was created with the discovery of mineral or hydrocarbon oils—a revolution almost too great for anybody outside the oil industry to appreciate. Vegetable and animal oil and fats are produced in great quantities for divers purposes, but the quantities of mineral oils obtained completely eclipse those of the fatty oils.

The mineral oil industry is often regarded as having its birth in the discovery made by James Young that petroleum could be obtained by the distillation of certain rocks, but there seems to be evidence that petroleum was known and used two or three thousand years before Christ. Excavators in Assyria have found excellently preserved walls cemented with bitumen which have stood probably thirty-five centuries.

According to modern translations of the Bible the words " slime " and " salt " have in many cases been substituted for the word " bitumen." Thus " slime had they for mortar " in the building of the Tower of Babel is perhaps the earliest reference to bitumen in the Scriptures. This interpretation places a new construction upon the fate of Lot's wife, who on looking back on the burning cities of Sodom and Gomorrah stumbled into a bitumen pit. According to the legend of Noah's ark bitumen from Hit, near Bagdad, was used to cover the ark.

The mythical conception of the origin of petroleum is interesting, as it constitutes the earliest record of the origin of petroleum. Prometheus was chained on the Caucasus Mountains for stealing the fire of heaven. During his captivity an eagle unceasingly devoured his liver, and afterwards vomited a black liquor which the Greeks called naphtha. Of course Caucasian petroleum was well known to the Greeks, as numerous references are made to it in ancient Greek literature.

In view of the developments of the modern Persian oilfield the words of Herodotus might claim attention as they are the first description of a regular petroleum industry. "At Ardericca is a well that produces three different substances; for asphalt, salt, and oil are drawn up from it in the following manner: It is pumped up by means of a swipe, and instead of a bucket half a wine-skin is attached to it. Having dipped down with the swipe a man draws it up and pours the contents into a reservoir, and being poured from this into another it assumes these different forms: the asphalt and the salt immediately become solid, but the oil they collect; it is black and emits a strong odour."

It is to the Romans that we are indebted for the oldest record of petroleum being used as an illuminating agent. The oil obtained from Agrigentum, Sicily, we are told, was used in the lamps in the temple of Jupiter.

About 1400 a concession was made for the collection of petroleum near Miano, in Italy, and about 1600 wells were made, 50 to 60 ft. deep, at Modena; and in the early part of the nineteenth century Genoa was lighted by oil from Amiano. The first occasion on which large scale petroleum distillation appears to have been practised was at Prague, in 1810, when the oil was distilled to obtain illuminating oil.

Whether the oil shale industry commenced in Great Britain the author does not know; but the fact that oil could be obtained from stone tells its own story in a patent which was granted late in the seventeenth century for a method for the production of pitch, tar, and oil from a kind of stone. The oil obtained was sold as "Betton's British Oil" to cure rheumatism.

The famous patent granted to James Young in 1850 is the landmark of the modern petroleum industry. Lord Playfair drew Young's attention to a viscous substance oozing into a coal mine at Alfreton, Derbyshire, which on examination proved to be crude petroleum. Young commenced to distil the crude oil to obtain the illuminating oil. At first the well yielded about 300 gallons per day, but in two years the flow ceased.

In 1854 the Pennsylvania Rock Oil Company came into existence to sink wells and to refine petroleum. In 1859 Colonel Drake, after many difficulties, succeeded in driving a pipe to a depth of 69½ ft., and tapped an oil-bearing stratum at Oil Creek, Pennsylvania. The daily output from the well was 840 gallons, which continued for a year. The drilling was actually undertaken by Old Billy Smith, as he was called. The names of Drake and Old Billy Smith are inseparable and have become historic. Drake failed to grasp the importance of his success, and, in his retirement, let pass the opportunity of gaining great wealth. He died after being in receipt of a State pension of $1500 per annum.

Very shortly after Drake's success there was a wild rush to Oil Creek to seek oil. Samuel Kier, a druggist of Pittsburg, who had been a very keen advertiser of petroleum or rock oil for medicinal purposes for some few years, realised the need for an efficient burner for the oil, and so he devised a burner with a detachable glass chimney, which would give a steady and smokeless light when burning the oil. From then onwards the industry grew rapidly until now it is one of the greatest industries of the world.

The petroleum industry in Russia has not been quite so romantic, though no less interesting. The history of the Baku oil-field is always associated with the fire-worshippers who for thousands of years have made pilgrimages to the eternal fires. The fires are simply burning natural gas which is being emitted from the earth. To us it is very commonplace to see gas burning, but to the heathen it must have appeared a very wonderful and awe-inspiring sight to see a fire not fed with visible fuel burning, and burning from time immemorial.

Marco Polo described the Baku oil industry as he found it in the twelfth century. He states that there was a great fountain of oil from which a hundred shiploads might be taken at one time. The oil was used for burning, and for this purpose was sought by people even from great distances. Evidently the oil trade was flourishing in those early days.

After the annexation of Baku by Russia from Persia, Peter the Great organised a systematic transportation of petroleum to the interior of Russia; but owing to the subsequent restoration of Baku to Persia the interests of the industry fell to other hands which worked for its advancement; for according to John Hanway's report (Report upon the condition of British trade in the Levant about the middle of the eighteenth century) the supply of oil was so abundant that it was used by even the very humblest of the people, and was even sent to India.

In the year 1800 about 120,000 barrels of oil were exported, the whole of the oil being obtained from springs. In 1801 the Russian Government controlled the industry, and it was not released until 1872, since when the industry has gradually developed.

Petroleum oil-fields are being discovered and worked in many parts of the world. Burma and Persia have already become great producing areas; Texas, California, Canada, Mexico, and the northern part of South America are firmly established sources of petroleum; many new fields are being explored with encouraging results, not the least of which are situated in England.

The magnitude of the industry may be gleaned from the output of 503,708,000 barrels of 42 gallons in 1917; in 1860 the world's production was only 500,000 barrels. Not only must we consider the magnitude as a whole, but some idea of the fertility of a prize well is important. Such a prize is the Mexican Eagle Oil Co.'s No. 4 Well which has had an output of over 100,000,000 barrels. Summers (*J. Inst. Pet. Tech.*, 5, 19, 1919, 147) estimates that the amount of capital invested in oil enterprise during the last fifteen years in limited liability companies is about £190,000,000.

CHAPTER II

OIL REFINING

Crude petroleum as it is obtained from the oil wells varies very largely in composition and character. Some crudes are almost pure hydrocarbons which only require to be separated by fractional distillation, whilst others contain large quantities of sand and water, together with sulphur, nitrogen and oxygen containing bodies which demand special treatment for their elimination.

In Mexico the crude oil is generally tolerably free from suspended matter, such as water and sand, owing to the fact that the oil is being exuded under great pressure, or in other words, is being pressed out of the oil-bearing strata; whereas in Java and California the crude is contaminated with water and sand, especially in Java, where mud volcanoes are encountered which, when burst, emit oil and gas intermixed with sand and water. The oil is stored in tanks, or reservoirs, to permit of the sand and water settling. Then it is taken to the refinery, which may be in the vicinity of the well, or through miles and miles of pipe to the refinery erected in some convenient centre. The pipes vary in diameter from 4 to 8 in., according to the character of the oil, etc., to be pumped through them. One of the Asiatic pipe lines is 576 miles in length.

In the refinery the crude is resolved into the many marketable products by fractional distillation and subsequent processes. In common with nearly all industries the methods involved in the manufacture of mineral oil products are hemmed with secrecy, but the general outline of procedure is common knowledge. The crude is heated in retorts and the resulting vapours are condensed at various temperatures, thus separating the hydrocarbons into various fractions according to their boiling-points. Broadly speaking the oil is divided by this process into three main groups, namely, inflammable, illuminating, and lubricating; it being, of course, understood that some crudes may give rise to any one or more of these groups according to their composition. These groups are divided into sub-groups according to the demands of the market. The inflammable group may be split into hydrocarbons of very low boiling-point which are used to a limited extent as local anæsthetics, light spirit for fat and oil extraction purposes, petrols for internal combustion engines ; the illuminating into the various grades of kerosenes and burning oils, and the lubricating oil group into the many varieties of oils used for lubrication and the manufacture of paraffin wax. Each commodity as it is prepared is refined according to the dictates of the market. The refining and working up of the products claim the skill of the chemist and the physicist as well as of the engineer.

The methods involved in the final purification are numerous, and vary with the class of oil undergoing treatment. Some oils are treated with concentrated or fuming sulphuric acid, subsequently with caustic soda; others respond to caustic soda treatment alone. An extremely valuable paper describing the action of concentrated sulphuric acid upon olefines is one by Brooks and Humphrey (*J. Amer. Chem. Soc.*, 1918, 40, 822–856), because it throws some light upon the imperfectly understood action of sulphuric acid upon mineral oils. The chief results of the action are polymerisation and the formation of secondary and tertiary alcohols and of alkyl hydrogen and dialkyl sulphates. It was found that no mono-olefine hydrocarbon yielded a tar when treated with acid cold. In the aliphatic series, with increasing molecular weight, the formation of alkyl sulphates and alcohols diminishes and polymerisation increases, hence the assumption arises that lubri cating oils which have been acid treated contain polymerised olefines. In cases where chemical treatment is undesirable adsorption methods are resorted to. The oil is treated with fuller's-earth, bauxite, magnesia, animal charcoal, etc., either alone or together as occasion demands. The adsorption process is often referred to as the filtration process, and oils subjected to this process as " filtered oils." Another method which has proved to be of great value, especially for refining illuminating oils, is that of Edeleanu, which consists of dissolving out certain substances from the oil with liquid sulphur dioxide, separating the liquid sulphur dioxide solution, and finally removing the sulphur dioxide from the oil.

Moore, Morrell and Egloff (*Met. and Chem. Eng.*, 1918, 18, 396–402) found that olefines and the lower aromatic hydrocarbons are soluble in liquid sulphur dioxide, whilst the paraffins up to decane are insoluble. The solubility of the naphthenes is governed by the temperature at which the extraction is made. The division of the hydrocarbons in the oil can be regulated by the control of the temperature.

Sulphur compounds are a very common and objectionable constituent in mineral oils. Various methods for their eradication are used; perhaps the Frash process is the best known. In principle it consists of treating the oil with finely divided metallic oxides with which the sulphur combines.

CHAPTER III

OCCURRENCE OF FATTY OILS

Fixed or Fatty Oils.—The use of fatty oils does not perhaps date back quite so far as do mineral oils; but when we consider that the mineral oils were more easily accessible in far distant days than were fatty oils, it is very creditable to learn from the Psalmist that oil was extracted in his day by man "to make him of a cheerful countenance." It is believed that oil was used for barter as well as for external application. There appears to be little doubt that the only fatty oil used was of vegetable origin, but it is not quite clear whether it was or was not olive oil. The value of the oil as a foodstuff was recognised by the ancients, and therefore became quite an established industry, but few records are available to mark its progress until its establishment in Holland; and subsequently in the fifteenth century mills sprang up in England. Pearson (*J. Roy. Soc. Arts*, 1919, LXVIII, 50) states that the first authentic documentary records of any factory date back to the seventeenth century and relate to a business at Evesham. To-day the home consumption is 600,000 tons per annum!

The vegetable oils which are used as lubricants are few in normal times, and since 1914 the range has been reduced owing to the demand during the Great War for edible fats and oils. Probably rape and castor are the only two oils which are employed extensively; copra, palm kernel, cotton-seed and olive have been used with success, but they are little in evidence to-day owing to restrictions; and the day may not be far distant when the rape and castor oil supplies will be largely absorbed by the margarine makers. Should this occur it is highly probable that our researches will have revealed our independence of vegetable oils; in fact, it is not improbable that that independence will be attained before the shortage takes effect, or in the meantime vast undeveloped oil territories will be tapped

The principle involved in the extraction of the oil is the same to-day as it was even before the dawn of the Christian era, namely, that of the expression of the oil from the fruit by pressure. Vitruvius, writing on farm buildings, gave details of a press-room in the year 30 B.C., and Pliny made reference to it in A.D. 77; and later, of course, we find the growth of the industry in Holland. Pascal, in 1652, was instrumental in the foundation of the hydraulic press such as is used to-day, but it was not until 1795 that the use of water was developed by Bramah, and perfected by Chambauvet in 1830. A few years later Falquire made a pressure developing 2987 lb. per sq. in. To-day the seed is crushed in vertical presses, a pressure of 1½ tons per sq. in., except for palm kernels and similar seeds, when a much greater pressure is required. The seed may be crushed cold, such as for the manufacture of pharmaceutical castor oil, or hot as for "firsts" castor oil. Sometimes the oil is extracted with solvents, and subsequently the petroleum spirit, or whatever solvent is used, is distilled off.

The purification of the oil was developed on the Continent to a greater extent than in this country owing to the demand for margarine, but lately the scale has changed and this country has made rapid strides. In 1914 only 2000 tons of margarine was made in England, but in 1919 it had risen to 10,000 tons; also the material had improved to an amazing extent in both flavour and feeding value.

The methods used to purify the oil demand skill and specially designed plant. In a few words the method is to treat the oil with caustic soda to remove free fatty acids, it is then washed, steamed, filtered with fuller's-earth to clarify it, and subjected to the action of superheated steam to remove odorous substances. The oil may then be treated with hydrogen in the presence of a catalyst to convert the oil into a hardened fat. This latter process is known as the hydrogenating process.

By far the greater portion of the oil-bearing seeds come from the tropics—palm oil comes principally from tropical Africa, likewise does palm kernel; coco-nut oil from many of the islands in the Pacific and Indian Oceans. Olive trees flourish on the Mediterranean coasts; castor beans come from India, Burma, Egypt, and South America; ravisine rape from South Russia; rape seed from East Indies and

South America, and cotton seed from the United States, India, and Egypt.

The sea, also, has proved to be a very profitable source of oil; in fact, the present dimensions of the fishing industry are due to the demands for fish oil for a great variety of purposes. The much-advertised cod liver oil for pharmaceutical purposes claims but a small proportion of the cod oil obtained. Very large quantities of fish oils are used for making soap, lubricating and burning oils, leather dressings, substitutes for linseed oil for paints, etc. The number of fish oils which are used in industry are approximately equal to the number of vegetable oils which are commonly employed, a fact which is not always realised.

Although cod is caught in abundance off the eastern coast of North America and Japan, perhaps the most coveted catches are made off the Norwegian coast, where an average catch of 30,000,000 cod is made in a season of a few months. From this number of fish about 900,000 gallons are obtained. Newfoundland contributes approximately 1,000,000 gallons and Japan 500,000 gallons per annum to the world's requirements.

The shark is hunted for its liver from which anything between 10 to 100 gallons of oil may be obtained, whilst livers have been obtained yielding 400 gallons. Whaling has had a remunerative past, but with the advent of mineral oils the output of whale oil has diminished to 3,000,000 gallons a year. The sperm whale yields an oil, or rather a liquid wax, which is peculiar to itself and therefore commands a relatively high price. The jaw of the porpoise yields an oil which is of considerable value for the lubrication of fine instruments because it does not readily gum, evaporate, chill, creep, or become rancid. The blubber of the porpoise yields an oil possessing commercial value.

CHAPTER IV

PHYSICAL TESTS

Flash Point.—The flash point of an oil is usually alluded to as the " open flash " or " closed flash," and it is very necessary to state which flash point is meant in recording data, especially in view of the fact that they are frequently confounded by buyers of oil. The " open flash," or flash point (open), is, broadly speaking, approximately 30° F. above the flash point (closed) of hydrocarbon lubricating oils. Although this may approximate to the truth in the case of hydrocarbon lubricating oils, yet it is obviously far from being accurate when dealing with crude hydrocarbon oils in which there may exist hydrocarbons of very different flash points. The flash point of a mixture of oils is not the flash point of the lowest flashing constituent, but is intermediate between the flash point of the oil with the highest flash point and the oil with the lowest flash point. A. Harker and W. F. Higgins, of the National Physical Laboratory, have shown that it is possible to calculate the flash point of a mixture of oils of low flash point to a considerable degree of accuracy. The author has applied the formula given by Harker and Higgins to oils with high flash points, and finds that it is tolerably correct.

The subject of flash point determination of oils of low flash point is treated very fully in a paper by A. Harker and W. F. Higgins, *Nat. Physical Lab. Collected Researches*, 8, 21–39 (1912).

The tables on page 12 show the flash points of mixed oils.

The formula given is

$$F = \frac{mxA + yB}{mx + y}$$

where F is the flash point of the mixture of oils whose individual flash points are A and B ; x and y are the respective proportions of the two constituents, and m is a constant.

For American oils . . . $m=0{\cdot}43$
,, Galician ,, . . . $m=0{\cdot}91$
,, Russian ,, . . . $m=0{\cdot}91$

Percentage of B by volume	Flash Points		
	B+E	B+A	B+C
100	59° F.	59° F.	59° F.
90	60·5	60·5	61
80	62	62	63
70	63·5	64	65·5
60	65·5	66	68
50	67·5	68·5	70·5
40	70	71·5	74
30	72·5	75	78
20	76	79	84·5
10	80·5	84	92
0	86	92	101·5

Percentage of A by volume	Flash Points of A+B	
	Found	Calculated
100	400° F.	—
80	382	380° F.
60	365	364
40	352	353
20	347	346
0	340	—

The flash point (closed) is that temperature at which the vapour from a substance will ignite in a closed vessel of definite dimensions and design. As no correlation between the flash point of a substance and any other physical or chemical property has been established, we are still in the unfortunate position of adopting an arbitrary figure obtained by using a standard apparatus, and performing the test according to definite rules. To emphasize the necessity of a rigid adherence to such rules some sources of error may be enumerated:

(1) The frequency of application of the test flame.
(2) Variations in the time of opening the shutter.
(3) Variations in the rate of heating.
(4) Variations in the depth of immersion of the thermometer.
(5) Variations in the size of the test flame.
(6) Variations in the rate of stirring.

Seeing how many vital points govern the accuracy of a flash point determination it is imperative that all flash point apparatus should be carefully examined prior to their adoption.

The points to be noted as made by Higgins specially refer to the determination of the flash point of oils with low flash points; but that should not reduce the care which should be taken when dealing with higher flash point oils. The author has investigated some of the possible conditions under which determinations are sometimes made.

Mineral oil used.
Ignition flame $\frac{1}{8}$ in. long.
Flame inserted every

12 seconds	401° F.
30 ,,	398
60 ,,	401

Rate of heating 4° C. per minute.

Rate of heating	Flame inserted	Flash point
2° C.	12 seconds	401° F.
8	12 ,,	401
12	12 ,,	401
2	30 ,,	402
8	30 ,,	401
12	30 ,,	402
2	60 ,,	406
8	60 ,,	406

Half the usual volume of oil used.
Flame inserted every

12 seconds	404° F.
60 ,,	406

Normal volume of oil. Flame ⅜ in. long.	
Rate of heating 4° C. per minute.	
Flame inserted every 12 seconds . . .	305° F.
Occasionally stirred	329
,, ,, Flame ⅛ in. long . .	397

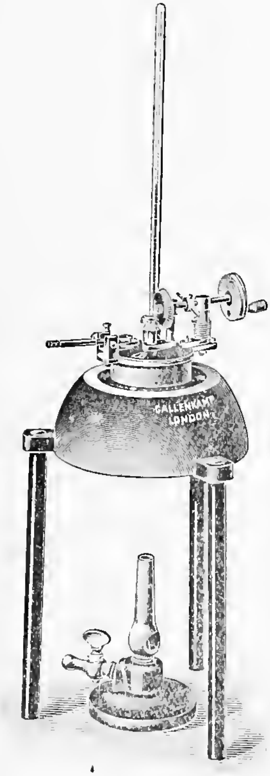
From these results it would appear as if the rate of heating up to 10° C. is without effect; the frequency of insertion of ignition flame up to 60 seconds interval gives normal results, whereas occasional stirring lowers the result slightly, but the size of the ignition flame is very important. The volume of oil even if it be only one half of the standard quantity is of small moment.

Although these observations may apply to the majority of normal lubricating oils it does not of necessity follow that they apply to all oils; in fact, when dealing with certain fatty oils the author has found that they do not.

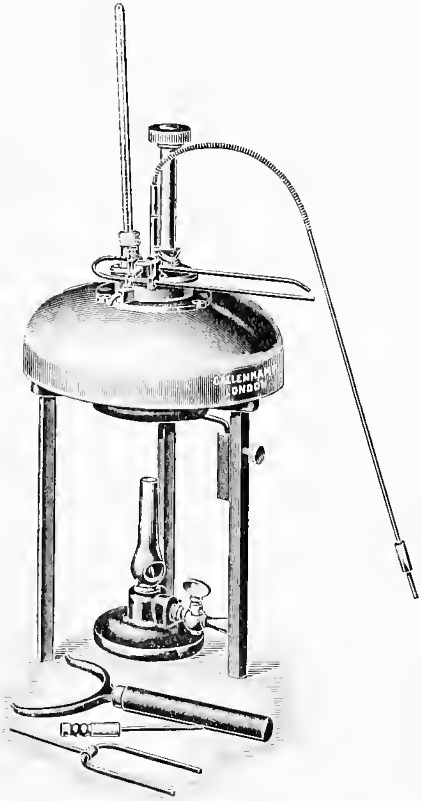
In the British Isles only the Gray Tester and the Pensky-Martens Flash Point apparatus are recognised. The difference between these designs of apparatus is small, as the illustrations show. The Pensky-Martens apparatus is perhaps the more widely adopted.

The oil to be examined is placed in the copper cup in such quantity as just to touch the mark, which will be found on the inside of the cup. The volume of oil required is approximately 75 c.c. Operators are recommended not to move the cup when the oil is in it, in order to avoid wetting the sides of the cup above the mark; so avoiding one of the possibilities of obtaining a low result. The cover with the thermometer fixed in position is then placed on the cup, and the injector burner lighted. The small flame should be about ⅛ in. long.

The apparatus is heated by a Bunsen burner. For oils of comparative low flash point it is advisable to place the wire gauze screen between the burner and the apparatus, but when examining oils whose flash point is above 300° F. the screen is usually unnecessary. Throughout the heating the oil must be constantly stirred. The stirring should be conducted rhythmically at a speed of approximately one revolution of the stirrer per second. If the stirring be slower a uniform temperature of the oil is not maintained; if, however, the oil be rapidly stirred splashing ensues, and sometimes the oil " creeps " over the top of the cup. The rise in temperature of the oil should be at the rate of 7° F. to 8° F per minute. When the temperature of the oil is approaching that at which the oil flashes the ignition burner is injected for about two seconds every half-minute until a distinct flash is seen within the cup; the flash is quite distinct if the test be performed in a darkened room. The vapour from some oils extinguishes the ignition flame up to a temperature within a few degrees of the flash point. As the temperature of the oil increases vapour is evolved, but in insufficient quantity to carburate the air in the cup to the flashing point; its presence is, however, readily detected by the sudden elongation of the ignition



Gray's Flash Point.



Pensky-Martens Flash Point.

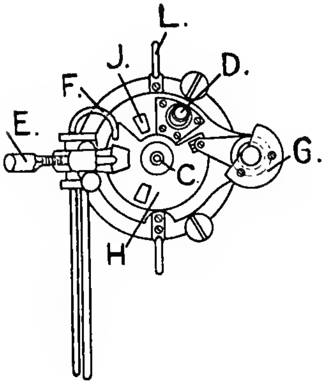
flame when it is injected. The flash takes place when the atmosphere inside the cup contains approximately 2% of oil vapour by volume. Some chemists prefer to heat the oil at a uniform rate of 4° C. per minute and insert the ignition flame every 12 seconds, the ignition flame being about $\frac{1}{8}$ in. in diameter. This method has an advantage over the previous method in that the possibilities of a "freaky" flash are diminished.

Oils containing minute quantities of volatile organic substances are liable to exhibit an irregular flash or flashes at a temperature below the regular and true flash point of the oil. Such a flash is termed a "freaky" flash because, although a small flash is observed, the intensity of the flash does not increase with increased temperature. Castor oil and oils containing water are very prone to give "freaky" flashes. If the ignition flame be extinguished, as it is sometimes, one meets with "freaky" flash points, not necessarily by virtue of the oil but through the ignition of the coal gas which has been injected into the apparatus from the ignition burner.

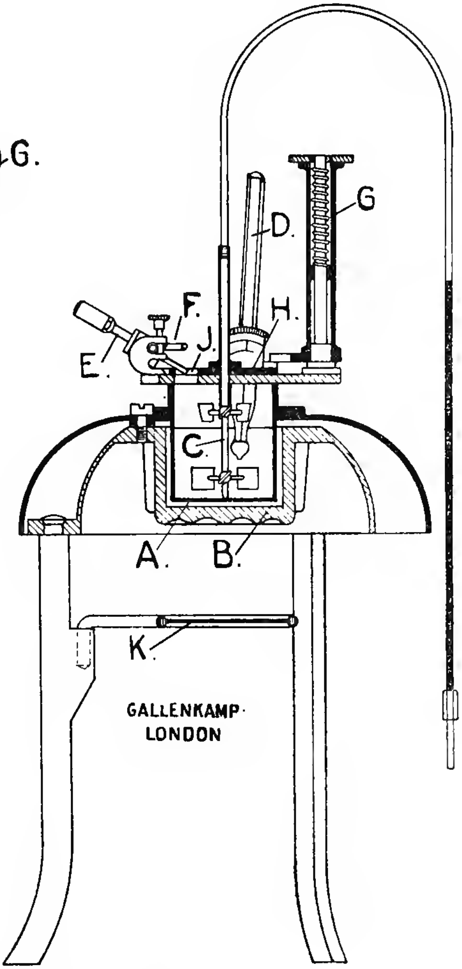
The presence of water in an oil may have a considerable influence upon the flash point, either by lowering or by raising it. The lowering of the flash point is probably due to the steam distillation of the lower members of the oil, whereas the raising is accounted for by the steam in the oil cup preventing the oil vapour from flashing. Considerable stress was laid upon this subject by Philip in a paper read before the Institution of Petroleum Technologists on October 4th, 1919, and in the discussion which followed. The following results obtained by independent observers show clearly the effect of water upon the flash point.

Description	Creosote Oil	Texas Oil	Turbine Oil
Water content . .	7·0%	1·5%	0·011%
Observed Flash Point	194° F.	241° F.	392° F.
	171	223	399
	190	241	396
	196	228	390
	189	232	401
	185	248	394
	174	—	394
	172	—	—
Variation . . .	25°	25°	11°

The removal of the water before testing can be done in several ways, including drying over calcium chloride, filtering hot through filter paper, heating the oil to 200° F. and passing a current of air through it. This last method, although open to possible objections, is perhaps the most convenient one and gives good results. The author does not favour the



A.	Oil Cup
B.	Heating Vessel
C.	Stirrer
D.	Thermometer
E.	Ignition Burner
F.	Pilot Burner
G.	Spring Handle
H.	Revolving Shutter
J.	Orifice
K.	Gauze Disc



Pensky-Martens Apparatus.

drying of the oil before making a test, because he believes it detracts from the value of the test.

After every determination the apparatus should be dismantled and very carefully freed from oil, not forgetting the underside of the shutter on the cover. Flash point determinations are best performed in a room where the light is subdued. Some oils appear to give a very undecisive flash; in such cases it is a matter of experience to determine the true flash point.

The **flash point (open)** can be conveniently determined upon the oil which has been used for the flash point (closed) by removing the cover from the apparatus and continuing heating. The oil can be efficiently stirred by a thermometer. A small flame about $\frac{1}{8}$ in. long is passed over the oil, without actually touching it, every half-minute until the oil flashes; or it can be determined by using a large crucible imbedded in a sand bath instead of the Pensky-Martens apparatus.

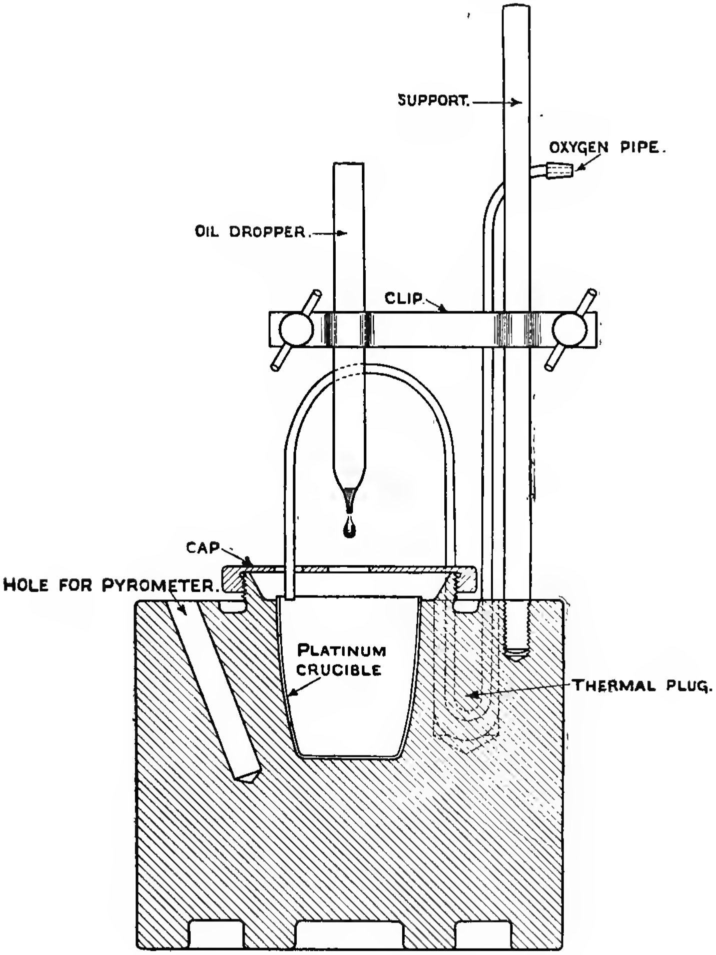
The **fire point,** or **fire test,** is that temperature at which an oil just commences to burn continuously. In performing this determination the thermometer should be watched carefully, because as soon as the oil begins to burn freely the temperature rises rapidly. The *modus operandi* of this test is exactly similar to that of the flash point (open). The fire point is approximately 60° F. above the flash point (open) in the case of oils whose flash point (open) is above 260° F.

The flash point of an oil furnishes no criterion whatever of the lubricating value of an oil; it does, however, give some clue to the composition of the oil, and its possible safety under given conditions. There is no correlation between flash point and specific gravity and viscosity, as the following table shows.

Viscosity in Redwood Secs.	Specific Gravity.	Flash Point (closed).
70 at 60° F.	0·870 at 60° F.	260° F.
1000 ,, ,,	0·905 ,, ,,	390
6000 ,, ,,	0·950 ,, ,,	310
12000 ,, ,,	0·900 ,, ,,	550

The ignition temperature, or spontaneous ignition temperature, is that temperature at which an oil will ignite when heated without the application of a flame. This test must not be confused with flash point tests as it is sometimes.

Several forms of apparatus have been designed, but the one described by Moore (*J.S.C.I.*, XXXVI, 109, 1917) is the best The instrument consists of a diffusion block of steel, 100 mm in diameter and 75 mm. in depth. The base has been turned in deep grooves to give a greater heating surface. In the centre of the upper surface is a hole into which fits exactly a platinum or nickel crucible. A cover screwed on the block



Apparatus for Testing Ignition Point.

protects the crucible from draughts. The cover is provided with two holes, one for oxygen or air inlet, and the other for the admission of the substance to be tested. The oxygen or air is passed from a container through holes drilled in the casting before entering the crucible, and is thereby preheated to the temperature of the diffusion block. The block is provided with a hole to fit the stem of a thermo-couple for registering the temperature of the instrument.

Oxygen is passed into the crucible at the rate of three bubbles per second after being passed through a potash tower and strong sulphuric acid. When the instrument has reached a constant desired temperature, one drop of the oil is introduced through the hole in the centre of the cover. If the temperature is above the ignition point of the oil, an explosion occurs; if below, nothing occurs. The ignition point is the lowest temperature at which the explosion follows the introduction of the substance.

Specific Gravity.—Specific gravity, or weight of unit volume, is determined by weighing a known volume of oil and comparing its weight with the weight of an equal volume of water. The comparison against water is made because the specific gravity of water is taken as unity. In order to do this conveniently a specific gravity bottle is weighed, then filled with distilled water and placed in a large basin containing water at a known temperature (60° F.) for about thirty minutes. When the temperature of the water in the bottle has acquired the desired temperature, insert the stopper, which is made from capillary tubing, remove the bottle from the basin by holding only the neck, to obviate the possibility of warming the water by the heat of the hand, and consequent loss through the stopper, and carefully dry the outside of the bottle and any water remaining on the top of the stopper, and weigh again,

Specific Gravity Bottle.

Hydrometer.

The difference in the two weighings is the weight of water; further, since 1 c.c. of water weighs 1 gm., the number of grams of water in the bottle is also the number of cubic centimetres it contains. Having thus ascertained the capacity of the bottle, it is filled with the oil to be tested as above described, after carefully drying it. The oil-filled bottle is weighed. The specific gravity or density is calculated from the formula

$$\frac{\text{Wt. of oil}}{\text{Vol. of oil}}$$

A convenient quantity of oil to take is about 25 c.c.

The simplest method for measuring specific gravity is by the hydrometer. A hydrometer is a tubular vessel weighted at the base to enable it to remain in a vertical position when placed in the oil, and provided with a scale marked with specific gravity numbers. The hydrometer is placed in the oil, whose temperature is known, and allowed to come to rest. The specific gravity is shown on the scale at that point at which the surface of the oil is coincident with a mark on the scale.

Viscosity.—Pending a better scheme of classification, lubricating oils are generally grouped according to their viscosity. Prior to the introduction of mineral oils such a classification was unnecessary, because engineers relied upon such oils as castor, rape and sperm, whose viscosity vary but little. The advent of the hydrocarbon lubricating oils created a great economy in the systems of lubrication, for it gave to the engineering world a class of oils from which a lubricant of almost any viscosity could be obtained. As the viscosity of fixed oils varies within narrow limits, viscosity determinations of such oils, providing the oils be pure, are of minor importance; but as it is now possible to obtain hydrocarbon lubricants of any desired viscosity, it is highly important to be able to make accurate viscosity measurements.

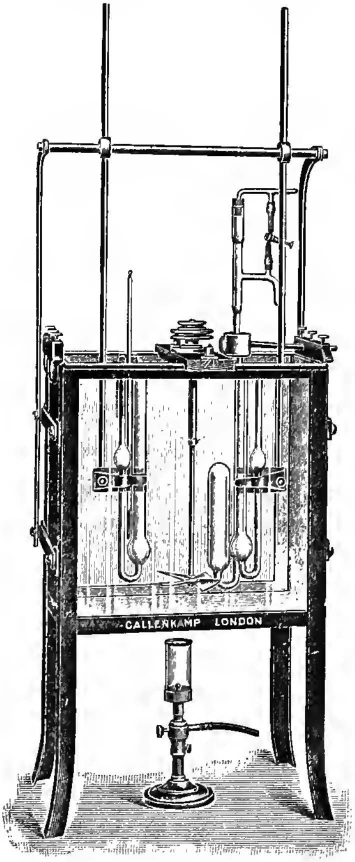
Viscosity may be very simply defined as "body" or "thickness"; for to the majority of people that is all that it conveys to their mind. More strictly it is a measure of the internal friction, and may be defined as the number of dynes required to move one square centimetre of substance over a layer of the same size and one centimetre distant with a velocity of one centimetre per second.

Maxwell's (*Phil. Trans.*, 1867) definition is—the viscosity of a substance is measured by the tangential force on unit area of either of two horizontal planes at the unit of distance apart, one of which is fixed, while the other moves with unit of velocity, the space between being filled with the viscous substance. This is the dynamical definition. When the effects of viscosity on the internal motions of a fluid itself are being considered it is often more convenient to use the kinematical definition. It is given in terms of μ, the coefficient of viscosity by the equation

$$\mu = \rho \nu$$

where ρ is the density of the substance, and ν the kinematic viscosity.

Viscosity, or fluid friction, is possessed by all liquids; that it is a question of friction may be readily illustrated by passing a liquid through a tube, and noting that the liquid contiguous to the wall of the tube moves more slowly than the liquid in the centre of the tube; evidently the friction between the liquid and the wall of the tube retards the flow of liquid, and each successive layer of liquid produces a retarding effect on the next layer. Lord Kelvin suggested that friction may be electrical in character, but to my knowledge no accepted explanation yet exists.



Ostwald Viscometers in Thermostat.

The experimental methods which have been used for viscosity determinations may be classified under three heads:

(1) By flow of the liquid through a tube.
(2) By motion in the fluid of pendulums, or vibrating discs.
(3) By the oscillation of spheres filled with the fluid.

Several instruments are in use in which the principle involved is either the flow of fluid through a tube, or the motion of a pendulum or vibrating disc in a fluid, notably amongst which may be mentioned the simplest form of viscometer, namely, the pipette; then we have the Ostwald, Redwood, and Doolittle viscometers. Helmholtz and von Piotrowski, *Sitzungsber. der Wiener Akad.* (1860), devised a method for viscosity determinations in which the third principle was involved.

Where scientific accuracy is desired, the Ostwald viscometer is recommended. The principle involved is the flow of fluid through a capillary. It is merely a U-tube of which one limb is wide and serves as a reservoir; the other limb is made with a capillary tube crowned with a bulb, attached to a short length of glass tubing. The essential feature of the Ostwald viscometer is the capillary, the size of which is chosen to suit the needs of a particular determination. A known quantity of liquid, usually about 5 c.c., is delivered into the reservoir tube, then the viscometer is fixed in a thermostat, whose temperature is adjusted to the temperature at which the determination is to be conducted. The temperature of the viscometer and liquid will acquire the temperature of the thermostat in about fifteen to twenty minutes. The liquid is drawn up through the capillary to a level above the mark above the bulb, and then allowed to flow freely through the capillary. The time taken for the liquid to flow from the mark on the glass tube above the capillary to another mark on the capillary tube is noted.

The specific viscosity is the comparison of the viscosity of the liquid under consideration with the viscosity of a standard liquid, e.g. rape oil, water, etc. The viscometer is calibrated with the standard liquid, by noting the time taken for that liquid to flow, under standard conditions, from mark to mark. The specific viscosity is calculated from the formula

$$V=n\,\frac{S_2D_2}{S_1D_1}$$

where

V = specific viscosity of liquid.
S_2 = number of seconds taken for flow of liquid.
D_2 = specific gravity of liquid.
S_1 = number of seconds taken for flow of standard liquid.
D_1 = specific gravity of standard liquid.
n = an arbitrary factor made by common consent. When the standard liquid is water $n=1$; when the standard liquid is rape oil $n=100$.

The Ostwald viscometer is valuable when only small quantities of material are available.

The determination of absolute viscosity with any degree of accuracy demands a considerable amount of care and skill in making physical measurements. The formula given by Poisseuille

$$\eta = \frac{\pi p r^4 t}{8vl}$$

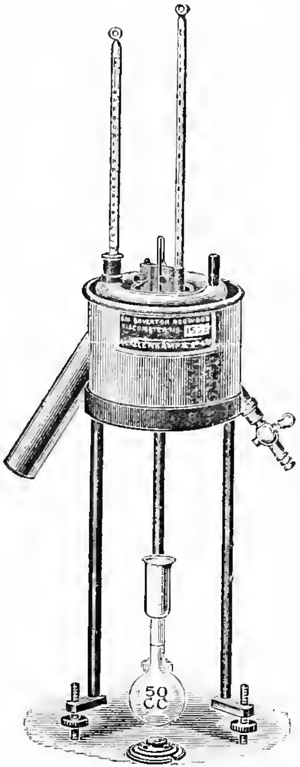
where

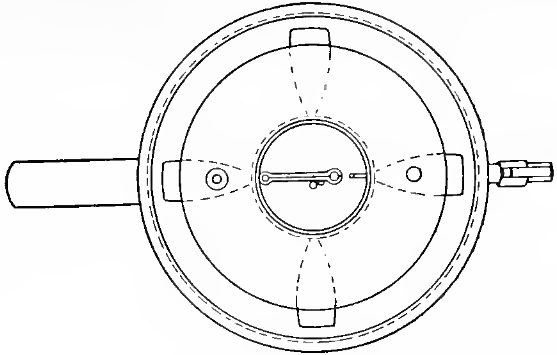
η = absolute viscosity.
p = pressure in grams per square centimetre.
r = radius of capillary.
l = length of capillary.
v = volume of fluid passed in t seconds.

is the basis of all modified formulæ for such measurements.

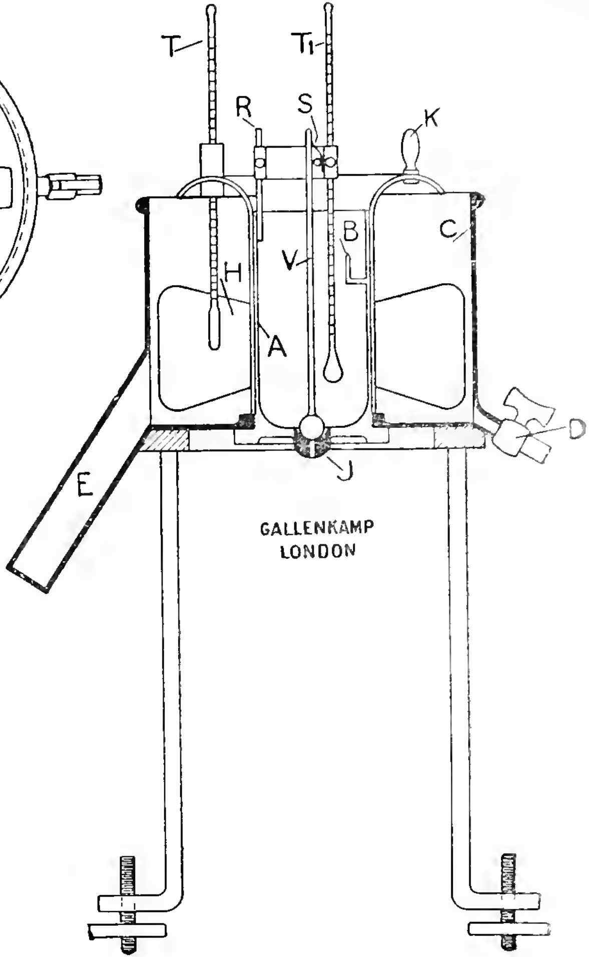
Redwood Viscometer.—The viscometer which is the most widely used in Great Britain is the Boverton Redwood type. It is based upon an instrument designed by C. Rumble. The Redwood viscometer is described in Sir Boverton Redwood's paper, *Journ. Soc. Chem. Ind.*, 1886, 125.

The instrument consists of a silvered copper oil cylinder, about 1⅞ in. in diameter, by about 3½ in. in depth, furnished with an agate jet. The exterior of the agate jet and its metal seating are made slightly conical, and the jet having once been fixed in position no dislodgment nor leakage can occur, even when the apparatus is used at high temperatures. The copper bath which surrounds the oil cylinder, and into which the oil cup screws, is of such a depth that the level of the bath liquid can be made to coincide with the level without any danger of overflow or splashing into the oil cylinder. A copper tube, closed at one end, projecting at an angle of about 45° from the side of the bath, near the bottom, provides a means of heating the bath liquid, and by the use of a revolving agitator the heated liquid rising from the copper tube can be uniformly distributed through the bath. The agitator, which carries a thermometer to indicate the temperature of the bath, is so constructed that splashing is prevented. The oil cylinder is furnished with a valve consisting of a small brass sphere attached to a wire, the sphere resting in an hemispherical cavity in the agate jet. A short standard, attached to the oil cylinder, carries a clip to support a thermometer in the oil. Inside the oil cylinder, and at a short distance from the top,





A.	Oil Cylinder
B.	Bracket
C.	Copper Bath
D.	Tap
E.	Heating Tube
H.	Stirrer
J.	Agate Jet
K.	Stirrer Handle
R.	Standard
S.	Thermometer Clip
T.	Thermometers
V.	Ball Valve



Redwood Viscometer.

is fixed a small bracket terminating in an upturned point. To compensate any slight deviations from the standard bore of the agate jet, corrections are made by a slight adjustment of the position of the bracket. This is done before the instrument is sold. No instrument should be purchased without an official certificate certifying its accuracy.

The instrument is supported on a tripod stand provided with levelling screws. A circular spirit level is provided to fit on the top of the oil cylinder.

Modus operandi.—The bath is filled with a suitable liquid to a height roughly corresponding with the point of the gauge in the oil cylinder. Water may be used for temperatures up to 200° F., and mineral oil for higher temperatures. The oil to be tested is placed in the oil cylinder, and its temperature adjusted to the temperature at which the determination is to be made, by regulating the temperature of the liquid in the outer vessel to such a temperature as will maintain the temperature of the oil in the cylinder at the desired temperature. In very hot weather the temperature of the outer liquid must be kept at 59·5° F. to maintain a constant temperature of the oil at 60° F., and at 60·5° F. in very cold weather. When the temperature of the experiment is 140° F., the outer liquid should be about 142° F.; when it is 200° F., the outer oil should be about 205° F., and when it is 250° F. the outer oil should be about 260° F. The oil in the cylinder is stirred by moving the thermometer backwards and forwards in the oil, but in such a manner as to avoid the formation of air bubbles, until the required temperature is attained. The outer liquid should be kept well stirred. The efficient stirring of the outer liquid and of the oil is the secret of rapid determinations. When the temperature has become constant, allow the oil to remain undisturbed for a few minutes to free itself from any currents created in the oil during the stirring. Fix the thermometer which is in the oil about half-way between the wall and the centre of the cylinder. Then the ball valve is lifted and secured on the thermometer holder, a stop-watch is started simultaneously and the time noted for the efflux of exactly 50 c.c. The 50 c.c. flask is placed in a vessel containing a liquid at the same temperature as the outflowing liquid so as to maintain the temperature of the liquid, or lagged with cotton-wool to obviate inaccuracies in the volume measurement through differences of temperature.

The capacity of the Redwood viscometer is about 135 c.c. The accuracy demanded for commercial purposes is probably in the neighbourhood of 3%, although in many cases a much larger margin is permissible, mainly because the viscosity of an oil for any given purpose is not accurately fixed owing to the varied conditions encountered in practice, and the human element. Until it is possible to standardise the selection of a lubricant more exactly it is not imperative to be too meticulous about the scientific accuracy of the viscometer. The Redwood instrument when carefully used should give an error not exceeding 1% on any two determinations, and an error of about 1% between any two instruments. Whether this instrument measures true viscosity for all times of efflux is open to criticism, especially when the time is less than about 40 seconds. For such short periods the capillary is too short to obtain a true viscosity effect, and therefore all oils appear to have the same viscosity at a temperature not exceeding 300° F.; whereas if the viscosity be measured in the Ostwald viscometer large differences are exhibited even at 500° F. This of course applies equally to the Engler and the Saybolt viscometers.

The instrument may be cleaned with paper, or some kind of cotton material which does not yield particles of fibre which might find their way into the agate jet. The author uses a very fine lawn such as is used for filtering oils.

The temperatures at which the determinations shall be made vary somewhat with the class of oil; generally engine oils are examined at 60° F. or 70° F. and 140° F.; whereas cylinder oils are examined at 200° F. and 250° F.; some exceptionally thick oils, such as tropical axle oils, are examined at 80° F.

The results may be recorded as the number of seconds taken for 50 c.c. of an oil to flow from a Redwood viscometer under standard conditions at a given temperature, or as "specific viscosity."

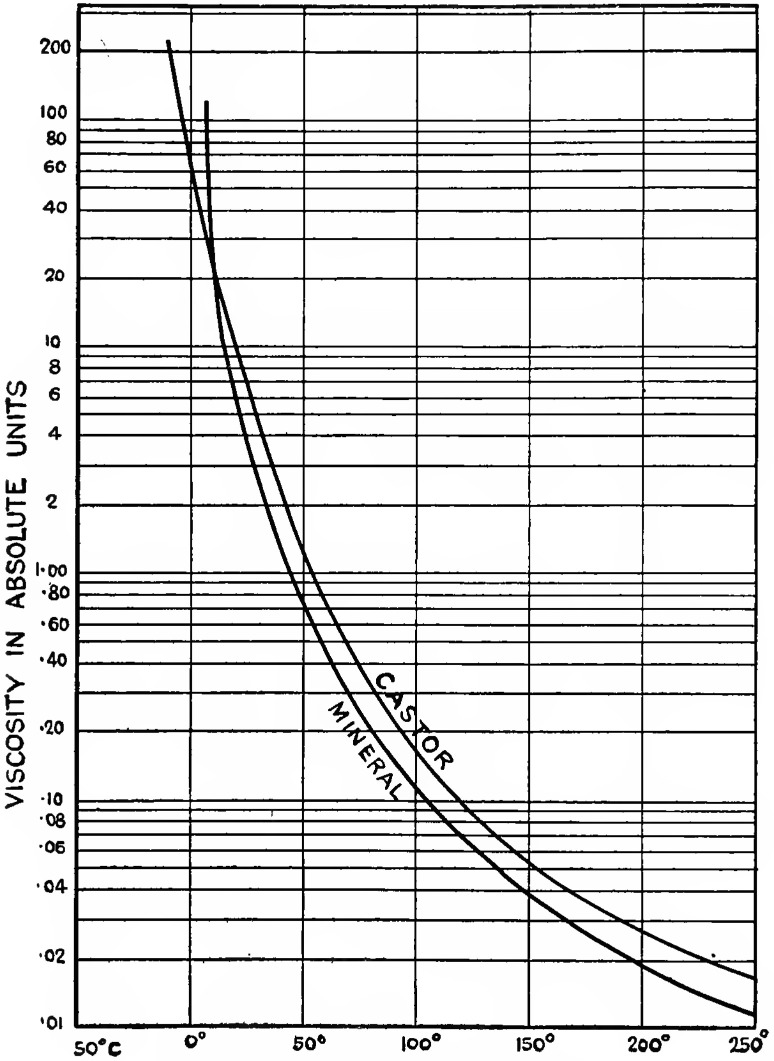
The calculation for specific viscosity is made according to the equation

$$V=n\,\frac{S_2D_2}{S_1D_1}$$

(vide page 23).

Redwood does not place much reliance upon results which exceed 3600 seconds, therefore the temperature at which the determination is made should be such as to keep the viscosity below 3600 seconds.

For commercial purposes, where the saving of time is desired, the time for a test may be reduced by noting the time taken for the efflux of less than 50 c.c., and multiplying the result by



Viscosity Determined in the Ostwald Viscometer.

a factor. The author has found the following factors from a large number of determinations.

Volume of oil collected		Factor
20 c.c.	..	2·80
25 ,,	..	2·25
30 ,,	..	1·85
35 ,,	..	1·50
40 ,,	..	1·3

Higgins' "Methods and Apparatus used in Petroleum Testing, Viscometry," *J.S.C.I.* (1913), 32, 568, states that over a range of 5 mm. on either side of the normal level the change in time of the outflow is proportional to the variations in level, the value being about 1·4% in the time for 1 mm. change of level on the Redwood instrument. Also that 1° of tilt from the horizontal is equivalent to a reduction of 0·3 mm. in the effective head. This corresponds to a change of 0·4% approximately in the resulting time of flow. The small circular levels supplied with the Redwood viscometers are usually sensitive to a tilt of about 0·2°, corresponding to an accuracy in the time of flow to 0·19.

In the Engler viscometer the accuracy under this heading is limited to about 0·2%.

From a very careful determination of the absolute viscosity of several oils he deduces the formula

$$\eta=\left(0{\cdot}0026\tau-\frac{1{\cdot}715}{\tau}\right)\delta$$

where

η = viscosity of liquid.
τ = time in seconds.
δ = specific gravity of liquid.

for calculating the viscosity of a fluid in absolute units when using the Redwood viscometer, and

$$\eta=\left(0{\cdot}001435\tau-\frac{3{\cdot}22}{\tau}\right)\delta$$

when using the Engler viscometer.

The accuracy of any individual commercial viscometer may be in the neighbourhood of 1%; but when one considers that a difference of 0·01 mm. in the mean diameter of the efflux tubes of the Engler, Saybolt-Universal and Redwood instruments may cause differences in the efflux times as great as

1·4%, 2·2%, and 2·5% respectively, and a difference of 0·1 mm. in the length of the efflux tube may cause differences of 0·5%, 0·7%, and 1% respectively, it is obvious that care must be taken with the jets to avoid damage. To compensate for these slight deviations in the dimensions of the oil cup or the capillary when made a compensating adjustment is made to the position of the needle-point gauge.

The Engler, Redwood, and Saybolt-Universal viscometers have efflux tubes of such large diameter and short length that the greater portion of the energy of flow is lost in the rapid passage of the liquid through the tube. In the Engler viscometer the energy used in overcoming viscous resistance within the tube, when water is the issuing liquid, is about 14% of the energy of flow imparted to the water. With a viscous oil about 95% of the energy of flow is absorbed in overcoming viscous resistance, hence the correction for energy of flow is small.

The Engler Numbers are only proportional to the absolute viscosity when the Engler Number is several times greater than that of water.

Engler Numbers can be converted into absolute units by the following factors:

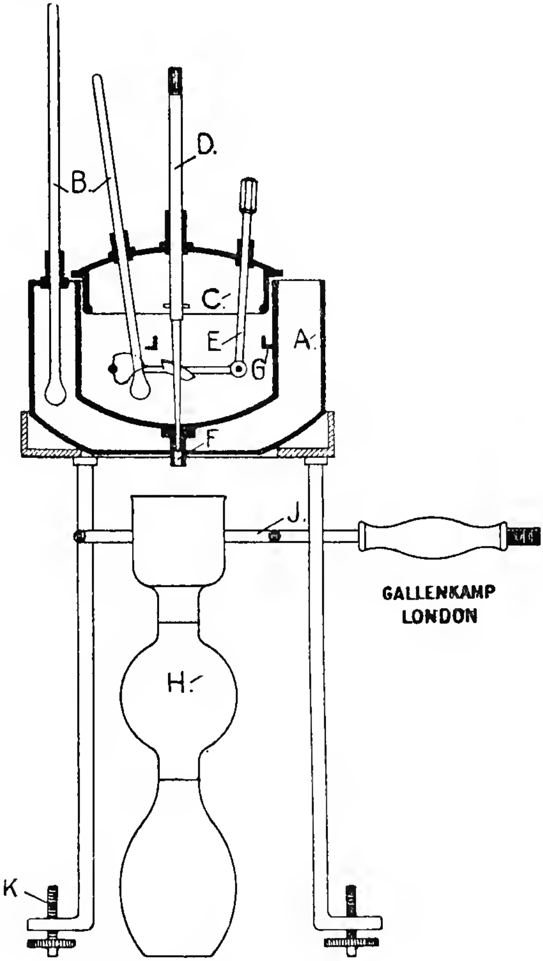
Engler Number	Dynes per sq. cm.
1	0·01006 × sp. gravity
2	0·1146 × ,,
5	0·353 × ,,
10	0·726 × ,,
20	1·46 × ,,
30	2·19 × ,,
60	4·38 × ,,

(Waidner, *Proc. Am. Soc. Test. Mat.*, Pt. I, 293, 1915).

The Engler Numbers of 5 or over are approximately proportional to the absolute viscosities.

Engler Viscometer.—In Germany and certain other countries the Engler instrument is used for viscosity determinations in technical laboratories. The instrument appears in forms in which the dimensions of the oil cylinder are uniform, but the mode of heating varies. The essential parts of the viscometer are a gilded oil container and a platinum jet.

This apparatus consists of two metal basins, one placed within the other, one serving as an oil reservoir, and the other as a thermostat. The former (the inner one) is closed by a lid, through which is put the thermometer B, for measuring the temperature of the oil. The thermometer for the water-bath is carried by a clamp with a holder fastened to the outer casing. The inner basin is fixed into the outer one by three bridges at the side, and the little discharge pipe F, closed by the valve-pin D which projects through the lid, serves as a support. Three needle-point gauges are fixed in



A. Thermostat
B. Thermometers
C. Cover
D. Valve
E. Stirrer
F. Jet
G. Level Gauge
H. Graduated Flask
J. Gas Burner
K. Levelling Screws

Engler Viscometer.

the inner basin at equal distance from the bottom for measuring the oil on the one hand, and on the other to serve for the correct adjustment of the horizontal position of the apparatus. When the reservoir is filled up to the gauge level it should contain 240 c.c. A tripod supports the apparatus. A measuring flask, H, having on its neck two marks, one registering 200 c.c., the other 240 c.c., is placed under the platinum jet when a determination is to be made. E is a stirring device.

To test the correctness of the apparatus the time taken for 200 c.c. of water at 20° C. to flow out of the oil reservoir, when it is filled up to the gauge points, is noted. Before removing the valve-pin the water in the oil container should be allowed to acquire a state of rest after being stirred. The time taken for the outflow of 200 c.c. of water at 20° C. should be 52 seconds. The same procedure is adopted when an oil is being tested.

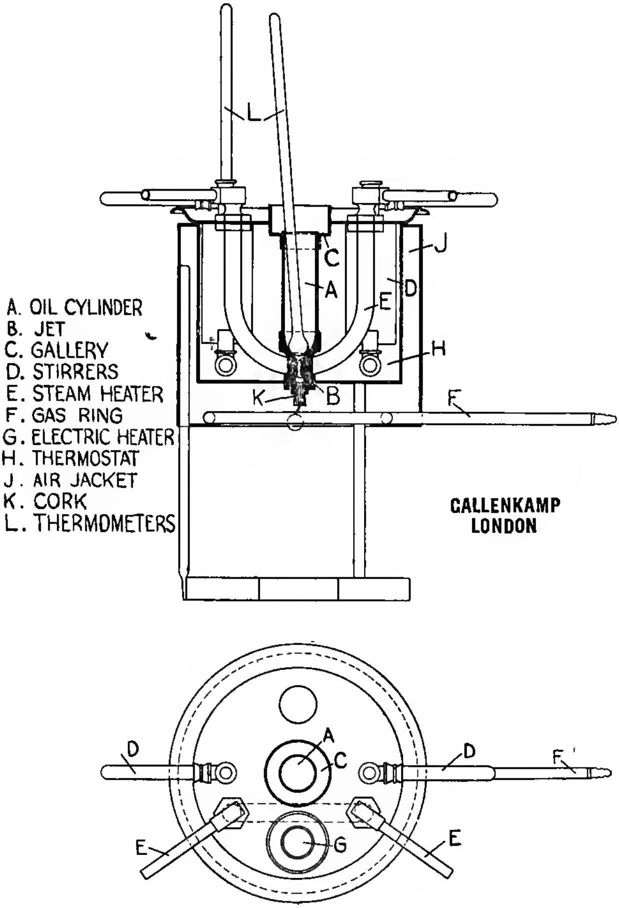
The Engler degree of viscosity is obtained by dividing the number of seconds required for the outflow of the oil by the time required for the outflow of water; e.g., suppose the time taken for an oil were 156 seconds, then the degree of viscosity would be 156÷52=3.

Owing to the capacity of the instrument, and to the large volume of outflowing oil to be measured, a determination often involves a considerable time, consequently Holde, *Mitteilung* 17, 63 (1899); Gans, *Chem. Rev.*, 6, 218 (1899), and Offerman, *Chem. Rev.*, 18, 272 (1911), have determined factors by which correct standard results can be obtained by using quantities of oil in the container less than that prescribed.

Vol. in container	25	45	45	50	50	60	120
Vol. run out .	10	20	25	20	40	50	100
Factor . .	13	7·25	5·55	7·3	3·62	2·79	1·55

The Engler viscometer is not well designed for the examination of fluids at temperatures above 212° F. In the first place the jet would become heated above the temperature at which the determination was being conducted through the slightly elevated temperature of the heating medium, and secondly it does not create sufficient differentiation between fluids at elevated temperatures. The temperatures at which it is customary to make the determinations are 20° C., 50° C., and 100° C.

Saybolt Viscometer.—This instrument finds favour in the United States of America, but it is not used in Great Britain, except perhaps by a very few workers. It is regrettable that



Saybolt Viscometer.

an instrument which is used by the large oil-producing undertakings in America should be so little known in this country, even if the instrument does not commend itself to our views.

It is stated that the instrument was at one time made in three forms: A, B, and C. "A" was the standard for testing at 70° F. Atlantic red, paraffin, and other distilled oils; "B" for testing at 70° black oils of 0°, 15°, 25°, and 30°, cold test, and other reduced oils up to, and not including, summer cold test oil; "C" was used for testing at 212° reduced, summer, cylinder, filtered cylinder, XXX valve, 26·5° F., and other heavy oils.

The Standard Universal viscometer is the one now used for testing cylinder and similar oils at 210° F.; reduced black oils at 130°; and spindle, paraffin, red, and other distilled oils at 100°. A. H. Gill describes the instrument as consisting of a brass tube, A, forming the body of the pipette provided with a jet B. The upper part of the pipette is surrounded with a gallery, C, which enables the operator to fill it to the same point every time. The pipette is contained in a water-bath, H, which can either be heated by steam or a ring burner, F. It may be used for testing cylinder, valve, and similar oils with bath at 212° and the oil at 210°; for testing reduced, black oils, bath and oil at 130°; for testing spindle, paraffin, red, and other distilled oils, bath and oil, at 100°. When used for testing at 212°, it may be used with either gas or steam alone or in combination. If with both, the steam may be introduced slowly, more for its condensation to replace evaporation than for real heating purposes, depending upon the gas flame to reach the boiling-point, and keeping it there during the operation of test. The bath vessel should always be kept full during a test, whether at 212°, 130°, or 100°. When used at 130° or 100°, gas alone is used to bring the bath to the prescribed temperature, and turned off during the test, the large size of the bath usually permitting making one test without reheating.

Its dimensions are as follows:

Diameter of overflow cup . .	51·0 mm.
Depth of overflow cup . . .	13·0 mm.
Diameter of pipette A . . .	30·0 mm.
Depth from starting head to outlet jet	113·0 mm.
Length of outlet jet . . .	13·0 mm.
Diameter of outlet jet . . .	1·8 mm.
Capacity of pipette A . . .	70 c.c.

Manipulation.—(1) Have the bath of water prepared at the prescribed temperature.

(2) Have the oil strained into one of the tin cups, in which cup it may be heated up to about the standard temperature.

(3) Clean out the tube with some of the oil to be tested by using the plunger sent with the instrument.

(4) Place the cork (as little distance as possible) into the lower outlet coupling tube just enough to make it air-tight, but not far enough to touch the small outlet jet of the tube proper (one-eighth to one-quarter of an inch may be enough).

(5) Pour the oil from the tin cup (again through the strainer) into the tube proper until it overflows into the overflow cup up to and above the upper edge of tube proper.

(6) Now again see that the bath is at the prescribed temperature.

(7) Use the thermometer sent with the instrument by stirring to bring the oil just to the standard temperature.

(8) Remove the thermometer.

(9) Draw from the overflow cup, with a pipette, all the surplus oil down to and below the upper edge of the tube proper. This ensures a positive starting-head.

(10) Place the 60 c.c. flask under and directly in line with the outlet jet, and as close to the coupling tube as is possible to permit of room for drawing the cork.

(11) With the watch in the left hand draw the cork with the right, and simultaneously start the watch.

(12) The time required in the delivery of 60 c.c. is the viscosity.

(13) Clean out the tube proper before each test with some oil to be tested.

(14) No drill or other instrument should ever be used in the small outlet jet of the tube proper.

60 c.c. of water at 20° C. flow out in 28·2 seconds.

The results obtained with this instrument are not the same in many cases as those furnished by A, B, and C instruments, but they seem to have been adopted by the trade generally.

The **expression of viscosity** is always a matter of some controversy, whether it be with one instrument or with the various types of viscometers used, therefore it is highly desirable to have one common method for the expression of results, or some ready means for converting the results obtained with one instrument into results which would be obtained with another instrument.

Although the Redwood viscometer is in daily use in this country there is no universal method for the expression of the results obtained; sometimes they are expressed in seconds, or as specific viscosity, where water is taken as unity, or rape oil at 60° F. = 100; less frequently a comparison is made against olive oil, tallow, glycerol, or even in absolute units.

On the Continent where the Engler instrument is favoured, a comparison with water is always adopted, and is known as the Engler Number. In the United States of America the results on the Saybolt Universal viscometer are expressed in time, although a comparison with water is being recognised.

The suggestion that results be expressed in terms of the viscosity of water, or in absolute units, naturally presents itself, especially as the absolute viscosity of water is accurately known, and so the two modes of expression are almost interchangeable. Until some such system be adopted conversion tables will be necessary.

VISCOSITY OF WATER IN C.G.S. UNITS BETWEEN 0° C. AND 100° C.

(Thorpe and Rodgers, *Phil. Trans.*, 185A, 1894)

Temp.	
0°C.	0·01778
5	0·015095
10	0·013025
15	0·011335
20	0·010015
25	0·00891
30	0·007975
35	0·00720
40	0·006535
45	0·00597
50	0·005475
55	0·005055
60	0·00468
65	0·004355
70	0·00406
75	0·003795
80	0·00356
85	0·00335
90	0·003155
95	0·002985
100	0·00283

CONVERSION TABLES

(*Proc. Am. Soc. Test. Mat.*, 15, 1, 288, 1915)

Saybolt Time Seconds	Factor Saybolt Time to Engler Number	Factor to Redwood Time
28	0·0357	0·95
30	352	95
32	346	94
34	342	94
36	337	94
38	334	93
40	330	93
42	327	92
44	323	92
46	320	91
48	317	91
50	314	90
55	308	90
60	302	89
65	297	88
70	293	87
75	289	86
80	286	86
85	284	86
90	282	85
95	280	85
100	279	85
110	276	85
120	274	84
130	272	84
140	271	84
160	269	84
180	268	84
200	267	84
1800	267	84

Multiplying Factors to Reduce Engler Number to Saybolt or Redwood Time

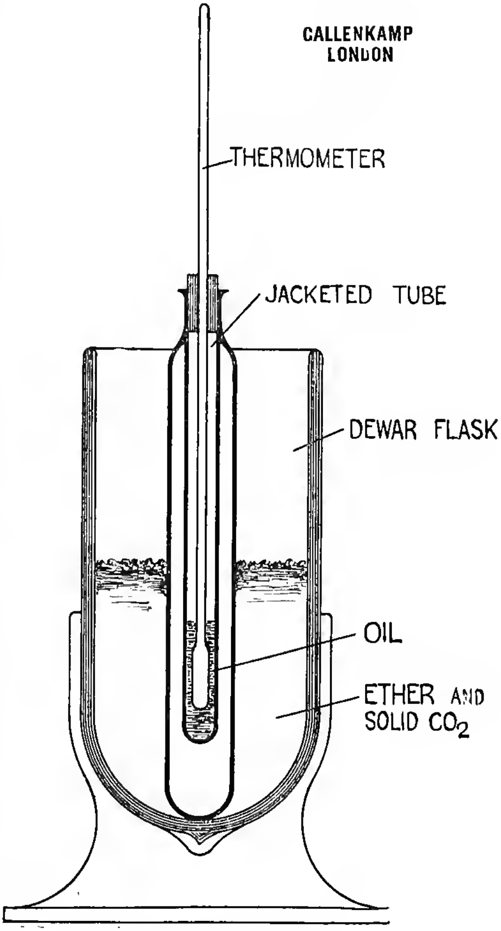
Engler Number	Factor to Reduce Engler Number to Saybolt Time	Factor to Reduce Engler Number to Redwood Time
1·00	28·1	26·7
1·05	28·4	27·0
1·10	28·8	27·2
1·15	29·1	27·4
1·20	29·5	27·6
1·25	29·8	27·8
1·30	30·2	28·0
1·35	30·5	28·2
1·40	30·8	28·3
1·45	31·1	28·5
1·50	31·4	28·6
1·60	32·0	28·8
1·70	32·5	29·0
1·80	33·0	29·2
1·90	33·5	29·6
2·0	33·9	29·7
2·1	34·2	29·9
2·2	34·5	30·0
2·3	34·8	30·1
2·4	35·1	30·2
2·5	35·3	30·3
2·6	35·5	30·3
2·7	35·7	30·4
2·8	35·9	30·4
2·9	36·1	30·5
3·0	36·2	30·7
3·5	36·7	30·9
4·0	37·1	31·1
4·5	37·3	31·2
5·0	37·4	31·2
6·0	37·5	31·3
8·0	37·5	31·3
50·0	37·5	31·3

Efflux Time for Engler Seconds	Engler Time / Saybolt Time	Engler Time / Redwood Time
50	1·83	1·92
52	1·81	1·90
54	1·79	1·89
56	1·77	1·88
58	1·76	1·87
60	1·74	1·85
62	1·72	—
64	1·71	1·83
65	—	—
66	1·70	—
68	1·68	—
70	1·67	1·81
75	1·63	1·79
80	1·60	1·77
85	1·58	1·76
90	1·55	1·75
95	1·53	1·74
100	1·51	1·73
105	1·49	1·72
110	1·48	1·71
120	1·46	1·70
130	1·44	1·69
140	1·43	1·68
150	1·41	—
160	1·40	1·67
180	1·39	1·66
200	1·38	1·65
220	1·37	1·64
300	1·36	1·63

Multiplying Factors to Reduce Redwood Time to Saybolt Time and to Engler Number

Redwood Time	Factor to Reduce Redwood Time to Saybolt Time	Factor to Reduce Redwood Time to Engler Number
28	1·05	0·0377
29	1·05	372
30	1·06	368
32	1·06	364
34	1·07	361
36	1·07	358
38	1·08	355
40	1·09	353
42	1·09	351
44	1·10	349
48	1·11	347
49	1·12	345
50	1·13	344
55	1·14	340
60	1·15	337
65	1·16	335
70	1·16	333
75	1·17	331
80	1·18	330
85	1·18	329
90	1·19	328
95	1·19	327
100	1·19	326
110	1·19	325
120	1·20	324
130	—	323
140	—	321
160	—	320
180	—	—
200	—	—
250	—	—
300	—	—
1500	1·20	320

Cold Test of lubricating oils is usually defined as that temperature at which the oil just ceases to flow. This definition should make a clear distinction between cold test and chill point, but since these must be factors common to both values some confusion is almost inevitable between the two.



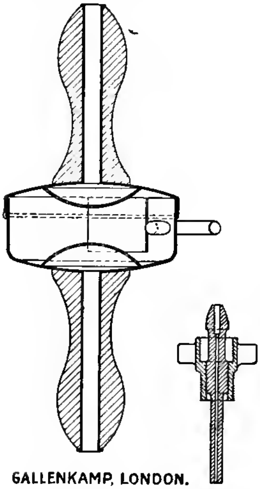
“Cold Test” Apparatus.

The test may be conveniently performed by pouring the oil to be tested into a test-tube of ½ in. diameter to a height of 1 in. A thermometer is inserted into the oil, and held in position by a cork. The tube is surrounded by a larger tube, to prevent too rapid cooling when the tube is placed in the cooling medium. The cooling may be effected by placing the apparatus in water cooled with ice, or in powdered ice, powdered ice and salt, or ether and solid carbon dioxide. As the cooling should not be effected too quickly the operator must decide which cooling agent to use. The tube is periodically withdrawn from the cooling medium, and inclined at an angle of about 45°, and noting the temperature at which the oil *just* ceases to flow. The temperature at which the oil *just* commences to flow should also be noted. The oil should not be stirred during the test.

Approximate Cold Test of Oils

Filtered Cylinder	40° to 100° F.
Engine	20° to 40°
Spindle	20° to 30°
Heavy Texas	0° to 20°
Light Texas	–50° to 10°

Solid carbon dioxide may readily be obtained by allowing CO_2 to escape from a cylinder of compressed CO_2, through a metal capillary tube fitted to the cylinder, into a metal receiver, in which the solid CO_2 will collect, or into a chamois-leather bag, although this is not quite so easy to manipulate.



Solid Carbon Dioxide Receiver and Capillary.

Dudley and Pease (*Am. Eng. and R.R.J.*, 69, 332, 1895) one-quarter filled a 4-oz. vial with the oil, cooled it until the oil became solid, then stirred the oil with a thermometer and noted the temperature at which the oil would flow.

Marten's (*Mitt. kgl. tech. Versuchstation*) method consists of placing the oil in a U-tube of 1 cm. in diameter, 16 cm. in height, and with a distance of 3 cm. between the arms, to a height of 3 cm. The tube is immersed in a cooling medium until the oil loses its fluidity, then a blast at a constant pressure of 3 cm. applied. The temperature at which the oil begins to flow is regarded as the cold test.

Another method which is used is to cool the oil, stirring all the time with a thermometer. The cold test is taken as that temperature at which the oil just ceases to drop off the thermometer when the thermometer is withdrawn.

Schultz's method is similar to Marten's, except that the oil is filled to a depth of 10 cm. into a U-tube 6 mm. internal diameter. The tube is maintained at the desired temperature for one hour, then the oil is subjected to a pressure of 5 cm.

of water. The distance moved by the oil in one minute is measured. The setting point being taken as that temperature at which the rate of flow of the oil is 1 cm. per minute.

The Mineral Oil Panel for Aircraft of the British Engineering Standards Association, of which the author is a member, has compared the U-tube method with the test-tube method. The test-tube used was 18 mm. diameter, and contained 3 cm. of oil.

Oil	Schultz	Tube	Difference
A	3° to 4° C.	—6·5° to —5° C.	9·5° to 9°
B	10° to 11° C.	6°	4° to 5°
C	10° C.	5°	5°
D	8° C.	5°	3°

By increasing the pressure on oil B to 10 cm. of water the cold test was reduced to 7° C. Hence it is possible that the U-tube method can be made interchangeable with the test-tube method.

Archbutt's method, as described in his book entitled *Lubrication and Lubricants*, consists of cooling 2 in. of oil contained in a tube 6 in. long and $\frac{3}{4}$ in. in diameter in a metal box containing a freezing mixture to a depth of 3 in. The metal box is enclosed in a wooden box provided with a lid, and packed with cotton waste, or other heat-lagging material. The temperature of the freezing mixture is taken by a thermometer placed in a similar tube containing an equal amount of a non-freezing oil. The tubes are left in the freezing mixture for one hour, then withdrawn and held horizontally to see if they will flow; if not, then a higher temperature must be maintained in the refrigerator; if they do, they must be cooled still further. After twenty minutes' exposure to the lower temperature they are re-examined and the temperature noted. By suitable additions of salt to ice a regular decrease in temperature can be made; a decrease of 5° F. can thus readily be made. If the oil be fluid at one temperature and is not at the 5° lower, the higher temperature is taken as the setting point, unless a closer approximation is desired, when the temperature of the freezing mixture is more carefully lowered.

The effect of temperature upon the storage of fatty oils is one which cannot be gauged in a few hours, therefore it is necessary to maintain conditions of cold for an extended period. The method used at the Aeronautical Inspection Directorate for castor oil is as follows:

A test-tube of about 18 mm. diameter shall be filled to a height of about 30 mm. with the oil. The tube shall then be lightly corked, the cork cut off level with the top of the tube and coated with Vaseline to exclude moisture. The tube shall then be placed in a vessel containing a solution of 22·5 parts of potassium chloride, of 100 parts of water, and fitted with a suitable graduated thermometer. This vessel is surrounded by another vessel, containing a mixture of two parts of crushed ice and one part of salt.

The solution in the inner vessel freezes at −10° C., which temperature is maintained until the whole is completely frozen. In order that the oil may be kept at as constant a temperature as possible the ice and salt in the outer vessel should be renewed every twelve hours and the inner vessel containing the freezing solution removed for a short time and its contents allowed to thaw.

The tubes containing the oil are examined at intervals of twelve to twenty-four hours, and the time at which the first signs of precipitation of small fat particles occur noted.

Chill Point.—Some oils contain substances which will separate at a definite temperature without the oil losing its fluidity. In some samples the determination is readily effected, but in others the separation may only occur after days or even weeks, consequently unless a special demand be made this test is very rarely made.

The manner in which this test is conducted varies considerably with different chemists; the main differences being in the time occupied in the determination and as to whether or not the oil be agitated. In certain classes of oil wide variations are found due to the want of standardisation of the method. A case in point was a petroleum oil which deposited solid matter at −10° C., but did not solidify, and when it was cooled to −12° C., after being at −10° for an hour, the deposit increased and still it remained fluid. The oil when cooled directly to −12° became solid. Evidently in the first case the solid matter was able to settle out, and leave the fluid portion free from solid matter, whereas in the second case the suspension of the solid matter caused the whole to have a solid appearance.

Similar phenomena are liable to occur with fatty oils.

Loss on Evaporation is perhaps one of those values which should appeal to the purchaser of oils from an economic point of view, but which even at the present time very rarely enters into specifications. For some obscure reason loss on evaporation is associated with flash point, therefore as flash point is generally demanded it is considered unnecessary to ask for the loss on evaporation. True, the higher the loss on evaporation the lower the flash point is almost a law, but the reverse is by no means a law.

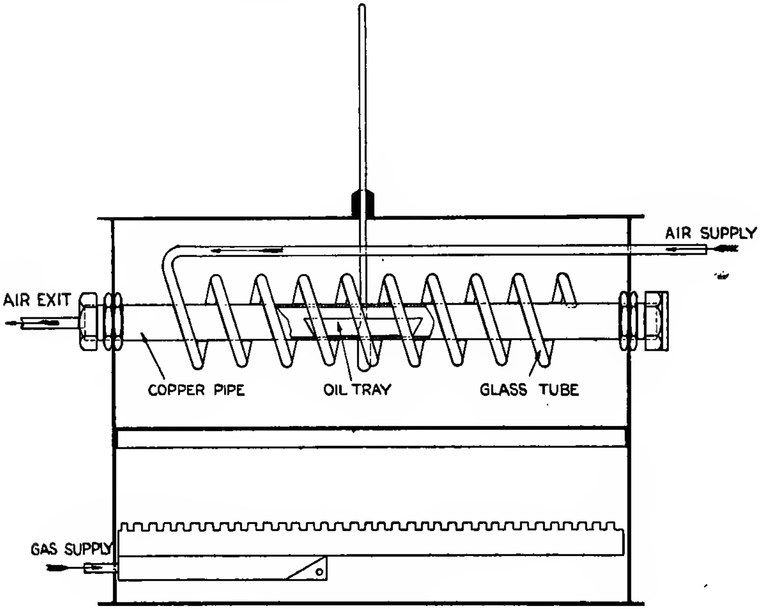
Oil	Loss on Evaporation at 100° C.	Flash Point (closed)
A	13%	275° F.
B	1·3	330
C	1·3	340
D	0·6	375
E	0·3	395
F	0·13	385
G	0·08	400

The delicacy of the Pensky-Martens flash point apparatus has been referred to under "Flash Point," consequently it is only necessary to state here that very small quantities of low flash point oil in a normally high flash point oil would materially lower the flash point of the mixed oil, but would scarcely influence the loss on evaporation. Suppose the oil F, in the above table, were fed into a superheated steam cylinder it would be useless as a lubricant, because it would be vaporised almost immediately. Now if a true superheated steam cylinder oil containing just sufficient petrol to reduce its flash point to 385° F. were fed, only the trace of petrol would vaporise, except for the normal vaporisation of the cylinder oil, and an adequate film of oil would be left. Cases such as this are obviously without the province of flash point, but within the sphere of loss on evaporation.

From the literature there appears to have been but little work done on the evaporation of oil. Archbutt has described a method for its estimation in his book, *Lubrication and Lubricants*, thus :

"The vaporimeter consists of a straight copper tube $\frac{7}{8}$ in.

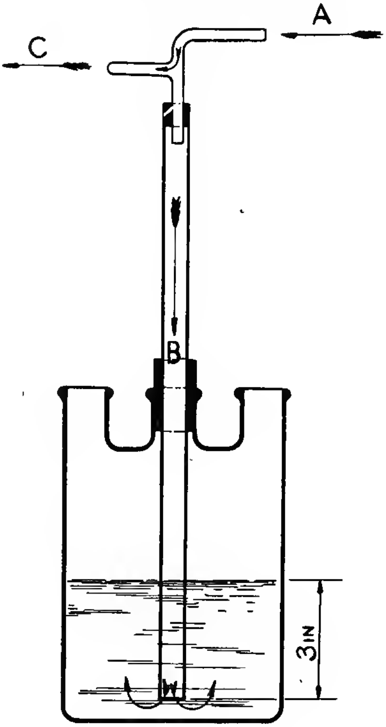
in internal diameter and 1 to 2 ft. long, having a branch tube $\frac{3}{8}$ in. in diameter and about 10 ft. long brazed into it near one end and coiled around the straight tube as shown in the figure. This tube and coil are fixed in a rectangular air oven made of tinned sheet-iron, the sides and top of which are covered with asbestos millboard. The oven is heated by a row of small gas-jets, and a thermometer is fixed with its bulb close to the middle of the wide copper tube. The ends of this tube which project beyond the oven are closed by brass screw caps, one of which, at the air exit end, is perforated and carries a narrow tube in the centre. Air or steam admitted to the coiled tube, after becoming heated in the coil to the temperature of the oven, passes over the oil in the wide tube and escapes through the short tube in the cap. The oil is contained in a platinum tray, 3 in. long by $\frac{1}{2}$ in. wide, by $\frac{1}{4}$ in. deep, which for convenience of manipulation is placed in a glass tube which just slides easily within the copper tube and serves as a carrier.



Vaporimeter.

The current of air is maintained at the constant speed of two litres per minute by means of the simple regulator. The air enters the regulator at A and a slight excess is kept continually escaping at the lower end of the wide tube B, which is immersed to a depth of 3 in. in water. The supply is taken from the branch C, the orifice of which is reduced until just large enough to pass two litres per minute against atmospheric pressure under the 3-in. head of water.

The quantity of oil used for the test is 0·5 gms. which forms a thin layer on the bottom of the tray and the oil is exposed to the air current for one hour."



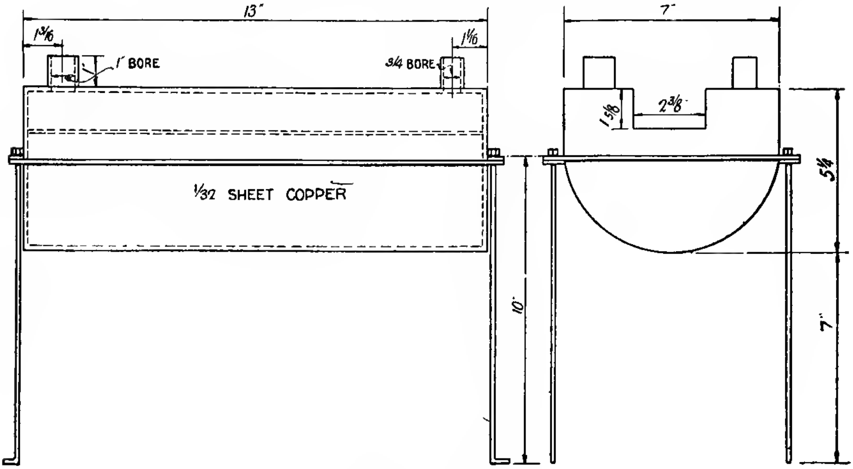
Air Regulator.

Michie's toluene vapour-bath method is used by the author, who has found it to give fairly good results provided it is protected from draughts and the toluene is not boiled too vigorously. It is described in *J.I.E.E.*, Vol. LIV, No. 258, 1916, by the Research Committee on Insulating Oils.

The apparatus consists of a copper bath fitted with a reflux condenser. The upper portion of the bath contains a trough, the ends of which can be closed by push-in doors. The oils to be tested (5 c.c.) are weighed into crucibles with flat bottoms and vertical sides 1½ in. in internal diameter. Difficulty has been experienced in obtaining such crucibles, consequently the author had glass ones made by Messrs. Gallenkamp and Co., Ltd. The crucibles are placed in the trough and surrounded to their upper edge with lead shot or small glass beads. A thermometer is inserted into the shot. By boiling the toluene a uniform temperature of oil at 100° C. is maintained. The heating is conducted for eight hours, at the end of which time the oil is reweighed and the loss per cent calculated.

An interesting account of evaporation tests is to be found in a paper issued by the Bureau of Standards in 1913, entitled "The Evaporation Test for Mineral Lubricating and Transformer Oil."

Demulsification Value is an extremely important consideration in judging the suitability of turbine and crank chamber oils. Into turbine oil reservoirs and crank chambers there is invariably a leakage of water which becomes mixed with the oil which if it does not separate readily gives rise to viscous emulsions, thereby diminishing the value of the oil as a lubricant in addition to the risk of choking the feed pipes. Furthermore, as it is imperative to remove the emulsion formed a quantity of oil is lost in the emulsion; if the emulsion be much the loss of oil through this medium becomes considerable. Emulsions may be troublesome by carrying salts from the water through the lubricating system and causing corrosion of the bearings and excessive sludging of the oil by setting up an e.m.f. between the bearing and the shaft.



Toluene Vapour Bath.

The power of an oil to form emulsion with water may be due to several conditions, but apparently the most important one in high-grade oils is the presence of suspended colloids.

A comprehensive paper on the subject is one by Philip read before the Society of Chemical Industry in June, 1915. He recommends that 500 c.c. of distilled water be stirred with 500 c.c. of oil at 100° C., the stirrer making 350 to 400 r.p.m. for five minutes. Then the mixture is run into a litre-graduated cylinder and allowed to stand for twenty-four hours. At the end of this period the amount of oil per cent which has separated is noted as the demulsification value. A turbine oil should have a value of at least 90%.

The apparatus used is perhaps too elaborate for laboratories where oils are not frequently examined, therefore the simpler test of shaking vigorously for one minute 100 c.c. of oil with 100 c.c. of water in a stoppered graduated cylinder will appeal to many chemists. The accuracy of the value obtained may be less, but it is sufficiently accurate for general purposes.

Specific Heat.—The specific heat of a substance is the amount of heat which is required to raise the temperature of one gram of a substance one degree centigrade at any temperature. Generally the specific heat of a substance increases with increase in temperature.

The method of determining the specific heat of a substance which has perhaps the widest application is that commonly known as the "method of mixtures." The substance whose specific heat is required is heated to a given temperature, and then rapidly immersed in a definite quantity of water, at a known temperature, contained in a calorimeter. From the rise in temperature of the water the specific heat is calculated. In addition to the amount of heat which is absorbed by the water a quantity is absorbed by the calorimeter, whatever its composition may be. To reduce this amount to a minimum the calorimeter is generally made of copper, or silver, or some other substance of low specific heat. A correction for this amount of heat is necessary.

Weight of substance	M
Weight of water	W
Weight of calorimeter	w
Initial temperature of substance	t_1
Initial temperature of water	t_2
Final temperature of water and substance	t_3
Specific heat of substance	s
Specific heat of calorimeter	σ

The heat lost by the substance is

$$M\ (t_1-t_3)\ s$$

and the heat received by the water is

$$W\ (t_3-t_2)$$

$$\therefore\ s=\frac{W\ (t_3-t_2)}{M\ (t_1-t_3)}$$

The amount of heat received by the calorimeter will be

$$w\ (t_3-t_2)\ \sigma$$

$$\text{Hence } s=\frac{W(t_3-t_2)+w\ (t_3-t_2)\ \sigma}{M\ (t_1-t_3)}$$

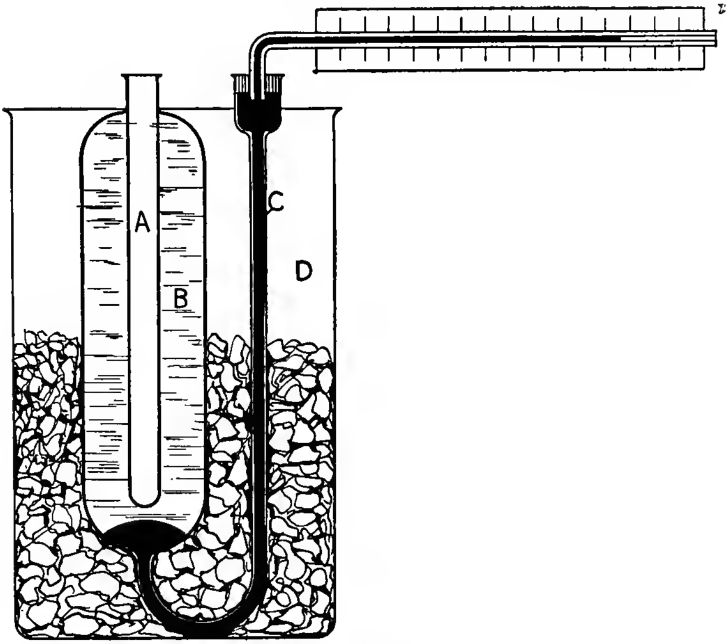
$$=\frac{(W+w\sigma)(t_3-t_2)}{M\ (t_1-t_3)}$$

For accurate determinations many precautions are necessary to prevent loss of heat of the substance during its passage from the heating medium to the calorimeter; the loss of heat from the calorimeter, either by conduction or radiation, etc.

Method of Fusion of Ice with Bunsen's Ice Calorimeter.—The tube A is sealed into a jacket tube B, to which is attached the limb C. The tube B is filled with well-boiled (gas-free) distilled water to a point below the base of the tube A, and C and the remaining portion of B is filled with mercury. A long capillary tube is fitted to C into which the mercury extends. The calorimeter is placed in a tall cylinder, D, and surrounded with powdered ice and water. For convenience a thermometer is suspended in A to ascertain when the apparatus has cooled to 0° C. A rapid current of air passing through D will ensure the rapid and even cooling of the water in B. When the water in B has cooled to 0° C. cooled ether is put into A, a rapid current of air passed through it to freeze some of the water in B. The position of the end of the mercury column in the capillary tube is marked. After all the ether has evaporated a weighed quantity of water at temperature *t* is dropped into A. A quantity of ice is melted by the heat of the water, consequently a contraction takes place of the water in B and the mercury recedes.

A similar weight of oil at temperature *t* is introduced to A after freezing some of the water in B as before, and noting the distance the mercury recedes.

This method eliminates the source of error created by the temperature of the surrounding atmosphere; further, there is only one temperature to take, namely, that of the substance, and there are no corrections for the calorimeter to consider.



Bunsen Calorimeter.

The mass of the substance (M), temperature of substance (θ), weight of ice melted (W), and the latent heat of fusion of ice (λ) must be known.

$$k=\frac{W\lambda}{M\theta} \qquad \lambda=80{\cdot}025 \text{ calories.}$$

The amount of ice melted is obtained by ascertaining the weight and volume of mercury drawn into the calorimeter when the ice melts. Winkelmann has found that the contraction in volume of 1 grm. of ice at 0° C. fusing into water at 0° C. is 0·0907 c.c. Hence for every calorie transmitted to the calorimeter by the substance there is a contraction of

$$\frac{0{\cdot}0907}{80{\cdot}025}=0{\cdot}0011339 \text{ c.c.}$$

therefore if the change in volume be V

$$k=\frac{V}{M\theta\times0{\cdot}0011339}$$

or

$$k=\frac{882{\cdot}304\,V}{M\theta}$$

(882·304 calories cause a contraction of 1 c.c.)

Weight of mercury corresponding to 1 calorie 0·01544 grm.

The weight of mercury drawn into the calorimeter

$$k=\frac{W}{M\theta\times0{\cdot}01544}$$

or by taking the density of mercury at 0° C. we have

$$k=\frac{64{\cdot}8978\,W}{M\theta}$$

The specific heat may be determined by an electrical resistance method, as described by Kohlrauch, *Lehrbuch der praktischen Physik*, 1910, 197. The oil is placed in a calorimeter suitably insulated. A Dewar flask makes an excellent calorimeter. In the oil is placed a resistance coil attached to a battery giving a steady current, which is measured. The oil must be constantly stirred, and the temperature taken by an accurate thermometer.

The specific heat is calculated from the equation

$$(ms+w)t=0{\cdot}239\times i^2rz$$

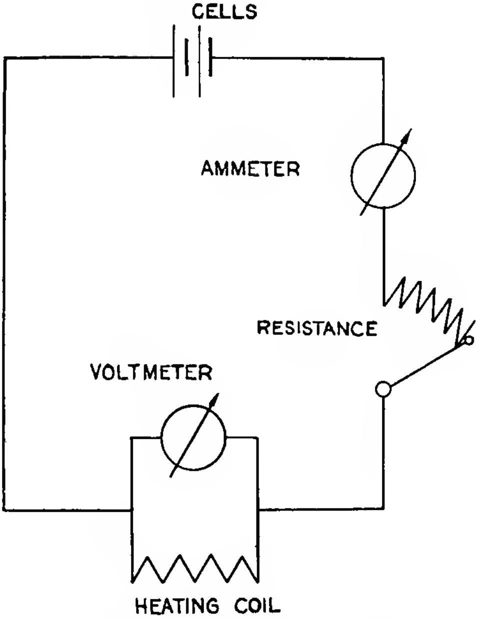
$$s=0{\cdot}239\left(\frac{rzi^2}{mt}\right)-\frac{w}{m}$$

where

Weight of oil	m
Water equivalent of calorimeter .	w
Time of heating	z
Temperature rise	t
Strength of current	i
Resistance of wire	r

Heat developed in one second is $0{\cdot}239i^2r$ calories, which is absorbed by the oil.

Prior to the work by Mabery and Goldstein (*Amer. Chem. J.*, 28 (1902), 66) very little appears to have been done upon the specific heats of the hydrocarbons which are found in mineral oils; the data which have been published are not very concordant. This is probably due to the very great difficulty in obtaining the hydrocarbons in a chemically pure condition, to the disturbing influences of small quantities of impurities in the hydrocarbon, and to the imperfect methods adopted for the specific heat determinations.



Electrical Resistance Method of Determining Specific Heat.

Bartoli and Stracciati (*Gazz. chim. ital.*, 14 (1884), 548, and 15 (1884), 417) give the specific heat of some of the paraffin hydrocarbons obtained from Pennsylvanian oil:

	Temperature	Specific Heat
C_6H_{14} . . .	16—37° C.	0·5042
C_7H_{16} . . .	16—37	4869
C_8H_{18} . . .	12—19	5111
$C_{10}H_{22}$ . . .	14—18	5057
$C_{14}H_{30}$ . . .	—	4995
$C_{16}H_{34}$ . . .	15—22	4963

Mabery and Goldstein determined the specific heats of those paraffin hydrocarbons from Pennsylvanian petroleum which are wholly liquid at 0° C. between 0° C. and 50° C.

	Boiling-point	Specific Heat
C_6H_{14}	68° C.	0·5272
C_7H_{16}	91	5005
C_7H_{16}	98	5074
C_6H_{16}	125	5052
C_9H_{20}	151	5034
$C_{10}H_{22}$	162	4951
$C_{10}H_{22}$	172	5021
$C_{11}H_{24}$	195	5013
$C_{12}H_{26}$	214	4997
$C_{13}H_{26}$	226	4986
$C_{14}H_{30}$	242	4973
$C_{15}H_{32}$	260	4966
$C_{16}H_{34}$	275	4957

The hydrocarbons examined were obtained by repeated distillation from Pennsylvanian oil and further purified by treatment with sulphuric acid, sodium hydroxide, and dehydrated by metallic sodium.

Methylene hydrocarbons obtained from Californian petroleum.

	Boiling-point	Specific Heat
C_6H_{12}	68° C.	0·5062
C_7H_{14}	98	4879
C_8H_{16}	119	4863
C_9H_{18}	135	4851
$C_{10}H_{20}$	160	4692
$C_{11}H_{22}$	190	4819
$C_{12}H_{24}$	212	4570
$C_{13}H_{26}$	232	4573
$C_{14}H_{28}$	244	4531
$C_{15}H_{30}$	263	4708

The higher hydrocarbons of this series were obtained from Pennsylvanian petroleum.

	Boiling-point	Specific Heat
$C_{16}H_{32}$	173° C.	0·4723
$C_{18}H_{36}$	202	4723
$C_{20}H_{40}$	223	4706
$C_{23}H_{46}$	260	4612
$C_{24}H_{48}$	272	4586

Although the higher hydrocarbons were obtained from a different source from the lower hydrocarbons there is a continuity in the specific heats, and as the specific gravity, refractive index, etc., of the higher hydrocarbons for Californian petroleum are in accord with those for Pennsylvanian petroleum it is probable that the specific heat is also.

Series C_nH_{2n-2} obtained from Texas petroleum.

	Boiling-point at 50 mm.	Specific Heat
$C_{14}H_{26}$	127° C.	0·4447
$C_{15}H_{28}$	142	4439
$C_{16}H_{30}$	162	4426

Series C_nH_{2n-4} obtained from Texas petroleum.

	Boiling-point at 50 mm.	Specific Heat
$C_{21}H_{36}$	218° C.	0·4560
$C_{25}H_{46}$	273	4650

The results obtained for the series C_nH_{2n-4} are unreliable as the quantities worked upon were very small and commenced to crystallise at 0° C.

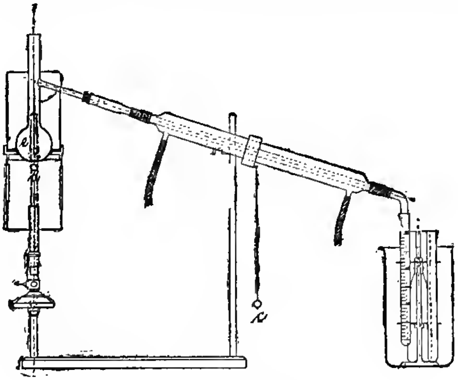
Crude Oils—	Specific Gravity	Specific Heat
Pennsylvanian	0·8095	0·5000
Berea Grit	7939	4690
Japan	8622	4532
Texas (Lucas Well)	9200	4315
Russian	9079	4355
Wyoming	8816	4323
Californian	9600	3980
Texas	9466	4009
Ohio	—	4951
Gasoline	—	5135

Californian oils vary from 0·3999 to 0·5016, average 0·4500. The specific heat is decreased with asphalt content.

Aromatic Hydrocarbons

C_6H_6	0·4672
$C_6H_5{\cdot}CH_3$	4984
$C_6H_5{\cdot}C_2H_5$	5347
$C_6H_5{\cdot}C_3H_7$	5653
$C_6H_3\ (CH_3)\ (^{1,2,4})$	5702

A number of oils whose specific heats have been taken have been calculated to unit volume instead of to unit weight, and it was found that approximately a constant figure was obtained.



Distillation Apparatus.

Distillation Test.—Distillation test is practically outside the sphere of lubricating oil examination except in dealing with oils which have been used in petrol and paraffin engines. Many times within the author's experience complaints have been made concerning the suitability of standard and well-reputed oils, for certain internal combustion engines, the complaints being that they rapidly lose their viscosity and become useless. True, a decrease in viscosity has resulted in a number of cases from the ingress of petrol or paraffin into the oil through the imperfect combustion of the fuel. In such cases it is necessary to determine the amount of fuel present. To do so 100 c.c. of oil are distilled from the distillation flask, which is attached to a condenser, at the rate of one drop from the end of the condenser per second. The fraction which is collected at a temperature not exceeding 150° C. is regarded as petrol, and that which is collected between 150° C. and 300° C. is paraffin. These temperatures are necessarily arbitrary, being governed by the distillation test temperatures of the petrol or paraffin which is being marketed. Nevertheless, as they are recognised in the petroleum industry it is convenient to regard them as standard figures.

The flask as standardised by Engler has a round bulb of 6·5 cm. with a neck 15 cm. long and 1·6 cm. internal diameter. The side tube is 10 cm. in length and is inclined downwards at an angle of 75°.

The flask used by Redwood has a bulb 2¾ in. in diameter, a neck ¾ in. in diameter by 5¾ in. in length, and the side tube is 2½ in. above the shoulder. The tube of the condenser should be 24 in. in length.

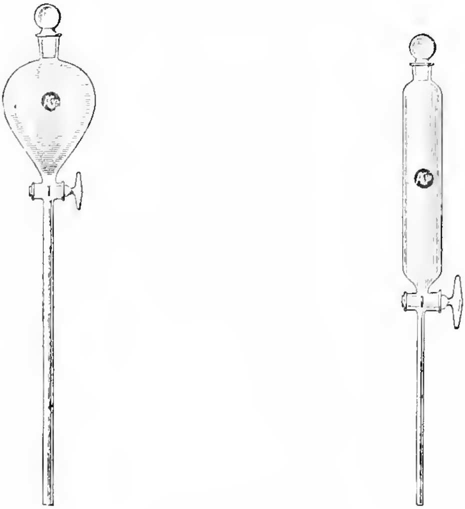
To protect it from draughts and uneven heating it is enclosed in a thin sheet-iron cylinder closed at the top, provided with an asbestos seat containing a 1½ in. circular perforation upon which the base of the flask fits. Asbestos is preferable to wire gauze because it reduces the possibility of superheating the vapour. The flask is fitted with a round bulb mercury thermometer, the bulb being about ½ in. below the side tube of the flask. A pendulum registering seconds is set in motion to enable the operator to regulate the rate of distillation with accuracy. When using a Redwood flask the heating is gradually increased, to maintain the correct rate of distillation, until the desired temperature is reached, but when using an Engler flask the flame is withdrawn at the desired temperature to allow the temperature to fall about 30° C. and then reheated; this cooling and reheating being continued until the distillate ceases to come over. The distillate is collected in a graduated cylinder.

CHAPTER V

CHEMICAL TESTS

Acidity.—Weigh accurately 5 to 20 grms. of oil in a small flask and add 20 to 50 c.c. of neutralised alcohol, warm gently, shake vigorously to dissolve the free acid and then titrate with $\frac{N}{10}$ NaOH in the presence of phenolphthalein.

In the event of difficulty being experienced in the titration through non-separation of the oil from the alcohol, the oil should be extracted three or four times with alcohol in a separating funnel. If the funnel be kept on a water-bath there should be no difficulty in effecting separation.



Separating Funnels.

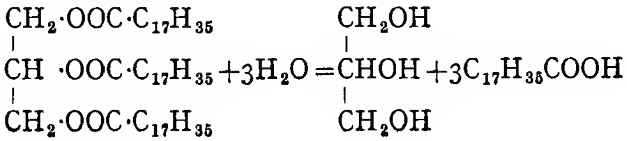
The result may be expressed either as milligrams of KOH per gram of oil, or as parts per hundred of oleic acid, or as parts per hundred of sulphuric acid, or sulphuric anhydride.

In view of the several free fatty acids which may be present in an oil it is obvious that the acidity shall be expressed in terms arranged by common consent. In reporting it is very necessary to state clearly that the acidity is calculated *as* so-and-so to obviate possible misinterpretation.

Oils which have been treated with sulphuric acid in the course of their preparation may inadvertently retain traces of this acid, hence it is always advisable to shake a known weight (100 grms.) of the oil with hot water in a separating funnel, and test the aqueous extract for free sulphuric acid by titrating with $\frac{N}{10}$ NaOH in presence of methyl orange. If an acidity be found the sulphuric acid should be determined gravimetrically, as water-soluble free fatty acids may be present.

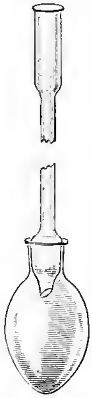
Saponification Value.—The saponification value of an oil is the number of milligrams of potassium hydroxide required to saponify one gram of oil.

The saponification or hydrolysis of a fatty oil, fat or wax is simply the process of decomposing the fatty oil, fat or wax into fatty acids and alcohols by treatment with a hydrolysing agent. The terms saponification and hydrolysis are not quite synonymous although they are frequently interchangeable. Saponification, as the word indicates, essentially involves the formation of soap, so that when a fat is decomposed into fatty acids and glycerol by an agent which is capable of combining with the liberated fatty acids, such as potassium hydroxide, to form soaps saponification is said to have been effected. If, however, the agent be not capable of combining with the liberated acids to form soaps then only hydrolysis has taken place. Suppose the agent be steam or an acid, which it is sometimes, no saponification could result, although hydrolysis would. The saponifying or hydrolysing substance is a medium for the addition of water to the fat.



$$\begin{array}{lcl} CH_2\cdot OOC\cdot C_{17}H_{35} & & CH_2OH \\ | & & | \\ CH\ \cdot OOC\cdot C_{17}H_{35} + 3H_2O & = & CHOH + 3C_{17}H_{35}COOH \\ | & & | \\ CH_2\cdot OOC\cdot C_{17}H_{35} & & CH_2OH \end{array}$$

Obviously the saponifying solution must become gradually weaker as the saponification proceeds, because it is being converted into soaps, whereas, theoretically speaking, an acid agent can hydrolyse an infinite amount of fat. This fact is of vital importance, especially in lubrication problems.


Saponification Flask.

The saponification value of an oil serves as a useful means in identifying it, or in determining its purity. True, it is not a fixed value, but it only varies within narrow limits, sufficiently narrow to be of service. Unfortunately more than one oil may have approximately the same saponification value, hence this value can only be used in conjunction with other data in the analysis of an oil.

Some chemists use the terms "Koettstorfer Number," or "Alkali Value," for "Saponification Value." A multiplicity of terms having exactly the same interpretation is unnecessary and misleading to those who are not in constant touch with the literature on the subject. Allen (*Comm. Org. Analysis*, Vol. II, 16) has introduced the term "Saponification Equivalent," which he defines as the weight of oil saponified by 56·1 parts of potassium hydroxide, or by one equivalent of any other alkali.

Hence saponification value per cent : 100 : : 56·1 : saponification equivalent

$$\therefore \text{ saponification equivalent} = \frac{5610}{\text{saponification value}}$$

(56·1 is the molecular weight of KOH).

The saponification equivalent of any glyceride (fatty oil or fat) is one-third of its molecular weight, and of an ester or a monohydric alcohol (wax) it is identical with its molecular weight. This will be readily understood when it is borne in mind that a glyceride gives rise to three molecules of an acid when it is saponified, whereas a wax only gives one molecule.

The saponification value per cent is one-tenth of the saponification value.

Determination.—About 1·5 grams are weighed accurately in a flask of about 200 c.c. capacity, then 25 c.c. of an approximately semi-normal solution of potassium hydroxide in alcohol are added. A long tube of not less than ¼ in. bore and about 3 ft. long is fitted to the flask to serve as a condenser for the alcohol. The flask is placed on a water-bath containing boiling water, or an electrically heated hot air bath adjusted to give a temperature of 100° C. The time required for complete saponification varies with different oils, but generally half to one hour is sufficient if the flask be frequently shaken. Simultaneously a similar flask containing 25 c.c. of the alcoholic potash solution is heated for the same period. This control experiment is done so that if the alcoholic potash should alter in strength during the heating through absorption of carbon dioxide, and dissolving the constituents of the glass, etc., a correction may be applied. Then the two flasks are cooled, a few drops of an alcoholic solution of phenolphthalein added to serve as an indicator, and the two solutions titrated separ-

SAPONIFICATION VALUES OF OILS FOUND IN LUBRICANTS

Class	Oil	Value
Vegetable	Cotton-seed	193–195
Semi-drying	,, "stearine"	195
,,	,, blown	220–260
,,	Rape	170–179
,,	,, blown	220–260
,,	Ravison	174–179
,,	Sesamé	189–193
Non-drying	Arachis	190–196
,,	Olive	185–196
,,	Castor	183–186
Marine animal	Cod	171–189
,,	Seal	189–196
,,	Whale	188–194
Terrestrial animal	Neatsfoot	194–199
,,	Sheep's foot	194·7
Vegetable fats	Palm	196–205
,,	Palm-nut	242–250
,,	Coco-nut	246–260
Animal fats	Lard	195·4
,,	Beef tallow	193–200
,,	Mutton tallow	192–195
Liquid waxes	Sperm oil	123–147
Solid waxes	Wool wax (Yorkshire grease)	102
,,	Beeswax	90–98

ately with semi-normal hydrochloric acid. Hydrochloric acid is better than sulphuric acid on account of its salt being soluble

Example:

Weight of flask	46·4434
,, ,, +oil . . .	47·6826
,, oil	1·2392

Control 25 c.c. KOH solution requires 22·7 c.c. $\frac{N}{2}$ HCl.

After saponification 25 c.c. KOH ,, ,, 14·9 c.c. $\frac{N}{2}$ HCl.

$$\text{Since 1 c.c. of } \frac{W}{2} \text{ HCl} = \frac{0{\cdot}0561}{2} \text{ grm. KOH,}$$

$$\text{Then } \frac{(22{\cdot}7 - 14{\cdot}9) \times 0{\cdot}0561}{2} = 0{\cdot}2184 \text{ grm. of KOH}$$

were required to saponify the oil.

i.e. 1·2392 grms. of oil required 0·2184 grm. of KOH
or 1·2392 ,, ,, ,, 218·4 mm. of KOH

$$\therefore \quad \text{1 grm. of oil would require } \frac{218{\cdot}4}{1{\cdot}2392} \text{ mm. of KOH}$$

$$= 176 \text{ mm. of KOH.}$$

Hence Saponification Value = 176.

There are a few fatty substances which are but imperfectly saponified by the above-described treatment. Such bodies must be saponified under pressure in a small, good bottle, provided with a rubber stopper which is securely fastened down with string. The bottle is heated inside a water-bath, but to prevent it from cracking by uneven heating it is advisable to place it on a perforated tin box-lid.

Great care must be exercised in performing this operation, in case the bottle bursts.

Determination of Fatty Oil in a Compound Oil.—The saponification value of the oil is first determined; then by a simple calculation the amount of fatty oil can be estimated approximately, thus:

$$\frac{\text{Saponification value (\%)} \times 100}{\text{Saponification value (\%) of fatty oil present}} = x \text{ \% fatty oil.}$$

It may happen, as it frequently does, that the saponification value of the fatty oil present is unknown. In such a case Gripper, *Chem. News*, LXV. (1892), 27, suggests the adoption of a saponification value per cent of 20, as being approximately the mean saponification value per cent of the common fatty oils.

Determination of Mineral Oil in a Compound Oil.—The oil is saponified in the usual way, except that the heating is continued for about three hours; the excess of potassium hydroxide is neutralised with dilute sulphuric acid, and then re-made slightly alkaline with potassium hydroxide. Ether is added to the flask to dissolve the unsaponified oil. Then the contents of the flask are very carefully transferred to a separating funnel. In order to ensure the complete transference of the contents of the flask into the funnel the flask should be washed out three times at least with small quantities of ether, then several times with distilled water, and finally with ether. The whole of the washings must be added to the main bulk in the funnel. This done, the funnel is stoppered, and shaken for a few minutes with an alternating circular motion. Should the shaking be done too vigorously the two solutions are liable to form an emulsion which is often difficult to disperse. On standing undisturbed the solutions will separate into two distinct layers, the upper layer being the ethereal solution of the unsaponifiable oil and the lower layer the aqueous solution of the soap, etc. The lower layer is run off. Where considerable accuracy is of importance the aqueous solution should be shaken with more ether, separated, and the ethereal solution added to the other separating funnel, but in works' laboratories this is frequently omitted. The ethereal solution is washed several times with warm distilled water, shaking and allowing to separate, as before, after each washing. If a troublesome emulsion should form separate the aqueous solution, as far as is possible, and add a little alcohol, shake and allow to stand. If the emulsion still remains wash twice with water and then with sodium chloride solution, warming if necessary, and finally with distilled water. What might appear to be a stable emulsion on the first washing with water may rapidly disperse after a few washings. After a little practice one can usually avoid the formation of emulsions. The washing should always be continued until the wash water is perfectly neutral. Then carefully drain off the last traces of water, and allow the ethereal solution just to fill the drilled portion of the tap key. This being done, dry the stem of the funnel with filter paper, and run the ethereal solution through about one gram of plaster of Paris, contained in a small filter, to remove any water which may be dissolved in the ether. The ethereal solution is collected in a weighed small flask. The funnel is washed several times with ether; each portion of ether used is passed through the filter also, care being taken to see that the whole of the interior of the funnel and edges of the filter are washed. The ether may either be distilled or evaporated (on a water-bath), and the residue dried in a water-oven, and weighed. The drying in the oven should not be prolonged more than is essential, because all mineral oils are more or less volatile, even at 100° C. No residue should require more than two hours' heating.

Difficulties will arise when one is dealing with burning oils or other hydrocarbons of low boiling-point.

Schreiber (*Journ. Am. Chem. Soc.*, 29, 74, 1907) prefers to dissolve the oil in benzene before adding the alcoholic potash, to effect a closer contact between the oil and the potash. For light-coloured oils the method may be used, but in the case of red and black oils it is useless, because the colour of the indicator when the solution is titrated would be masked.

A mathematical discussion of the saponification of fats has been published by Treub (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, 20, 35–63). He gives equations to explain the different course of the saponification in different surroundings.

It is commonly, but erroneously, assumed that mineral oils are inert toward caustic alkali, and therefore do not possess a saponification value. This assumption has led to many misunderstandings, and even disputes, which have been extremely unfortunate. The author has found great difficulty in obtaining concordant results when determining the saponification value of mineral oils even under varying conditions. The saponification value of hydrocarbon oils of the lubricating oil group is usually less than 4. This may seem low, but in the case of compound oils, containing only a few parts per cent of fatty oil, it is sufficient to create grave errors. A black compound oil was examined in the author's laboratory, and was found to contain about 7% of fatty oil by the usual saponification method; this result was found to be 2% too high by other methods. Other samples of a similar class of oil were found to contain 8% to 9% of fatty oil by the saponification method, whereas they only contained 5%.

In order to obviate such errors as this the author invariably determines the fatty acid and the glycerol content of compound oils, and from these results calculates the amount of fatty oil present. The mineral oil is always determined by ether extraction after saponification of the oil to check the result.

Determination of a Fatty Oil in a Compound Oil by estimating the Glycerol content.—Five to ten grams of the compound oil, according to the amount of fatty oil present, are saponified with an excess of alcoholic potash, the actual amount being immaterial. Boil for about three hours under a reflux condenser, then remove the condenser, and boil off the alcohol; when all the alcohol has evaporated re-dissolve in boiling water, and acidify with dilute sulphuric acid to liberate the fatty acids. This solution is very prone to "bump," hence it is advisable to add a small piece of glass rod to ensure steady ebullition. Boil until the aqueous layer is perfectly transparent, then filter as rapidly as possible, taking care to keep the filter full the whole time, and so avoid the risk of the oil and fatty acids leaking through the filter; wash with boiling water until the washings are free from sulphuric acid. The filtrate containing the glycerol is concentrated, and the free sulphuric acid removed by the addition of barium carbonate. After the addition of the barium carbonate care must be taken to avoid spitting as the solution approaches dryness. The dry mass is extracted with alcohol-ether (1 : 1), the solution being passed through a filter, to arrest any solid matter, into an acetylation flask. The alcohol-ether is distilled off and the impure glycerol is boiled with about 5 c.c. of acetic anhydride and about 1 grm. of anhydrous sodium acetate for 1½ to 2 hours.

An acetylation flask is simply a round-bottomed flask fitted with a ground-in glass air condenser.

Anhydrous sodium acetate is prepared by gently heating the crystalline salt until it just fuses without blackening.

Allow the acetylated product to cool, add carbon dioxide free water and warm, not boil; when solution is complete filter into a 1500 c.c. flask. The acetic acid in the filtrate is *exactly* neutralised with 2% sodium hydroxide solution; then a known quantity of 10% sodium hydroxide solution of known strength is added, and the solution is boiled gently under a reflux condenser for half an hour to hydrolyse the triacetin. Triacetin being volatile in steam it is essential that complete condensation of the steam is effected. Cool and titrate the excess of sodium hydroxide.

Weight of oil . . . . 19·6000 grms.

25 c.c. 10% NaOH require 118·1 c.c. $\frac{\text{HCl}}{2}$

After hydrolysis 113 c.c. $\frac{\text{HCl}}{2}$ were required

$$118{\cdot}1 - 113 = 5{\cdot}1 \text{ c.c.}$$

1 c.c. $\frac{\text{HCl}}{2}$ corresponds to $\frac{0{\cdot}092}{3} \times \frac{1}{2}$ grms. glycerol

$$\frac{5{\cdot}1 \times 0{\cdot}092 \times 1}{3 \times 2} = 0{\cdot}0782 \text{ grm. glycerol.}$$

Fatty oil contains 5% (approx.) of glycerol

$$\frac{0{\cdot}0782 \times 100}{5} = 1{\cdot}56 \text{ grms. fatty oil}$$

19·6000 grms. oil contain 1·56 grms. fatty oil

$$100 \text{ grms. oil contain } \frac{1{\cdot}56 \times 100}{19{\cdot}6} = 8\%.$$

Determination of a Fatty Oil in a Compound Oil by the Fatty Acid content.—Sometimes it is convenient to estimate the fatty acids in a compound oil and then to calculate the amount of fatty oil present therefrom. As most fatty oils contain about 95% of insoluble fatty acids it is not always necessary to know the nature of the fatty oil present. There are some exceptions, however, the most important being :

Dolphin jaw	66·3
Palm-nut	88–91
Coco-nut	82–90
Butter	86·5–90
Sperm oil	60–64
Wool wax	59·8

A quantity of oil, containing about 1 to 2 grms. of fatty oil, is saponified, the excess of alcoholic potash nearly neutralised, the mineral oil extracted with ether in the usual way, and the aqueous extract containing the soap and glycerol is evaporated to dryness to remove the alcohol. It is preferable to remove the alcohol after extracting with ether rather than before.

The dry soap is redissolved in water, the solution boiled, and the fatty acids liberated by dilute sulphuric acid. When the fatty acids have separated completely they are filtered, observing the special precautions previously given. The fatty acids are transferred to a weighed dish, washing the filter paper with ether. The acids are dried in a water-oven, and weighed

Iodine Value.—Hübl's (*J.S.C.I.*, 1884, 641) method is to allow a solution of iodine and mercuric chloride in alcoholic solution to act upon the oil for a number of hours in the dark.

The iodine solution is prepared by dissolving 25 grms. of pure iodine in 500 c.c. of 95% alcohol, and the mercuric chloride solution by dissolving 30 grms. of mercuric chloride in 500 c.c. of 95% alcohol. The mercuric chloride solution frequently requires filtering after having been made. The two solutions are kept separately until they are required for use, then equal volumes are mixed and allowed to stand for twenty-four hours before use.

The strength of the iodine solution so mixed is ascertained by titrating it with sodium thiosulphate solution, made by dissolving about 24 grms. of sodium thiosulphate crystals in 1000 c.c. of water.

The sodium thiosulphate solution is standardised by weighing exactly 3·8657 grms. of pure potassium bichromate, dissolving it in distilled water and making the solution up to 1000 c.c.; 1 c.c. of the bichromate solution will liberate exactly 0·01 grm. of iodine. Approximately 10 c.c. of a 10% solution of potassium iodide in water are poured into a 500 c.c. glass-stoppered bottle, together with 5 c.c. of strong hydrochloric acid; then exactly 20 c.c. of the bichromate solution added when 0·2 grm. of iodine are liberated according to the following equation:

$$K_2Cr_2O_7 + 14\ HCl + 6\ KI = Cr_2Cl_6 + 8\ KCl + 7\ H_2O + 3I_2$$

The solution is allowed to stand for a few minutes after well shaking, then 300 to 400 c.c. of water are added, and well mixed with the contents in the bottle. The solution will be of a dark yellow colour, which is gradually discharged when the thiosulphate solution is slowly added from a burette. When the colour has become very faint, add a few drops of freshly made starch solution to produce the blue "starch iodide." Then continue to add the thiosulphate solution until the blue colour completely disappears on shaking. The volume of thiosulphate solution added is noted. From this the strength of the thiosulphate solution in terms of iodine is calculated.

Volume of bichromate solution used . . .	20 c.c.
1 c.c. $K_2Cr_2O_7$ solution liberates . .	0·01 grm. I
∴ 20 c.c. ,, ,, ,, . .	0·2 ,,
Volume of thiosulphate solution added .	17·6 c.c.
Hence 17·6 c.c. of $Na_2S_2O_3$ solution oxidise .	0·2 grm. I
∴ 1 c.c. ,, ,, ,,	0·01136 ,,

The iodine value of an oil is that weight of iodine which is absorbed by 100 grms. of oil.

It is determined by taking an accurately known quantity (0·2 grm. of a drying oil, 0·3 grm. of a semi-drying oil, 0·4 grm. of a non-drying oil, 1·0 grm. of a solid fat, wax, or mineral oil) and dissolving it in 10 c.c. of a suitable solvent, e.g. chloroform, carbon tetrachloride, glacial acetic aid, etc., but not ether, contained in a 500 c.c. stoppered bottle; then add exactly 25 c.c. of the alcoholic iodine-mercuric chloride solution, shake, and allow to stand in the dark overnight, after replacing the stopper and moistening it with potassium iodide solution to absorb any iodine which might volatilise. A control test is made simultaneously by proceeding as above, except that no oil is used.

At the expiration of about eighteen hours 20 c.c. of 10% potassium iodide solution is added to each bottle, the first few drops being used to wash the stopper, and after a thorough agitation to dissolve the excess of iodine 300 to 400 c.c. of water are added, and titrated with the sodium thiosulphate solution as described above. From the difference between the number of cubic centimetres required for the control and the test can be calculated the amount of iodine which has been absorbed by the oil.

Weight of oil taken	1·0536
Volume of iodine solution used . . .	25 c.c.
Volume of $Na_2S_2O_3$ required for control .	39·4 c.c.
Volume of $Na_2S_2O_3$,, ,, test .	26·4 c.c.
Difference	13 c.c.

1 c.c. $Na_2S_2O_3$ = 0·0119 grm. iodine
13 c.c. $Na_2S_2O_3$ = 0·1547 ,, ,,
1·0536 grms. of oil absorbed 0·1547 grm. iodine
100 ,, ,, ,, 14·67 grms. ,,
Iodine Value = 14·67.

Wij's method is a modification of Hübl's method, and is preferred by some chemists because of the greater stability of the solutions used, and the shorter time required for complete absorption of the iodine by the oil.

The iodine solution is made by dissolving 7·9617 grms. of iodine trichloride and 8·6670 grms. of iodine separately in warm *glacial* acetic acid, mixing the two and making up to a litre with acetic acid after cooling.

The procedure is then exactly the same as with Hübl's method except that the time is reduced to six hours, or even less. It is essential, however, that all solvents are tested with potassium bichromate and conc. sulphuric acid; if they reduce it and produce a green solution they should be rejected.

Hanus recommends the use of iodine bromide instead of iodine trichloride, but his recommendation has not found favour.

Iodine Values

Class	Oil	Value
Vegetable . .	Cotton-seed .	108–110
Semi-drying . .	Rape . .	94–102
,, . .	,, blown .	60–90
,, . .	Ravison . .	101–122
,, . .	Sesamé . .	103–108
Non-drying . .	Arachis . .	83–100
,, . .	Olive . .	79–88
,, . .	Castor . .	83–90
Marine animal .	Cod . .	154–181
,, .	Seal . .	127–193
,, .	Whale . .	121–146
Terrestrial animal .	Neatsfoot .	69–76
,, .	Sheep's foot .	74
Vegetable fats .	Palm . .	51–57
,, .	Palm-nut .	13–17
,, .	Coco-nut .	8–10
Animal fats . .	Lard . .	46–70
,, . .	Beef tallow .	38–46
,, . .	Mutton tallow .	35–46
Waxes . .	Sperm oil .	81–90
,, . .	Wool wax .	17–28

Radcliffe and Polychronis (*J.S.C.I.*, 1916, XXXV, 341) found that the iodine value of mineral oils varied with the method employed. The three methods are compared in the table, the comparison being made on a two-hour test.

Sp. Gr.	Hübl	Wij's	Hanus
0·905	10·8	23·7	30·9
0·925	14·0	34·4	36·0

The effect of temperature is not great

	0° C.	10°	20°
Hübl .	8·9	9·0	10·9
Wij's .	20·9	22·6	23·7
Hanus .	25·7	27·9	31·0

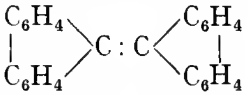
but time has a marked influence

Hours	Hübl	Wij's	Hanus
2	10·7	23·7	30·9
4	10·7	25·6	33·3
8	11·6	29·9	33·9
18	12·9	31·7	35·9
48	13·2	32·4	38·1

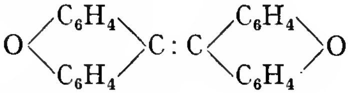
The Hanus method was found to be unreliable, inasmuch that slight differences in the amount of bromine lead to varying results.

From these figures it is perfectly evident that the absorption of iodine when determined under these conditions is somewhat irregular, and cannot be relied upon to measure the degree of unsaturation of the hydrocarbons in the oil. In fact, mineral oils differ in constitution from vegetable and animal oils, therefore it does not follow that because the degree of unsaturation can be measured in fatty oils that the same method will give equally satisfactory results with mineral oils. The power of an unsaturated group to unite with bromine depends upon the influence of its adjacent groups in the compound. Tetraphenylethylene $(C_6H_5)_2C:C(C_6H_5)_2$ is unsaturated, yet it does not combine with bromine, whereas diphenylethylene $(C_6H_5)_2C:CH_2$, and its methyl derivatives $(C_6H_5)_2C:C$

$(CH_3)_2$ do. Blitz (*Annalen*, 1897, 296, 231, 263) has shown that although tetraphenylethylene does not combine with bromine the closely allied compound tetraphenylene-ethylene



does combine with bromine. Its oxide



only combines with difficulty.

These examples of stereoisomerism serve to illustrate that iodine absorptions are of limited value unless the constitution of the compounds under test are known. Since mineral oils are complex mixtures of complex compounds of very uncertain constitution it is not surprising that difficulties should be encountered.

HÜBL AND WIJ'S METHOD COMPARED

Oil	Sp. Gr. at 15·5°C.	Hübl	Wij's
American—			
Cylinder .	0·875	10·2	22·8
Lubricating .	0·901	9·9	30·5
Spindle . .	0·901	10·8	34·0
Cylinder (black)	0·900	13·9	30·9
Russian—			
Cylinder .	0·914	9·9	22·0
Engine . .	0·904	6·4	16·8
Spindle . .	0·899	4·5	14·4
Scotch—			
A . . .	0·873	31·6	56·8
B . . .	0·890	24·5	49·8
C . . .	0·902	19·5	43·6

The **bromine value** has largely been abandoned in favour of the iodine value, but for mineral oils it may be that it has advantages over the iodine value. From the tables it will be observed that the Hübl method and Wij's method do not give identical results, therefore one or both are giving incorrect values. All that these methods determine is the amount of iodine which is absorbed, and do not differentiate between the amount of iodine which is added to the unsaturated compounds and the amount which is substituted in the saturated hydrocarbons. The bromine test can be made to measure both individually, and therefore possesses a distinct advantage in this respect.

The author has compared the bromine test with the Hübl iodine test. The bromine solution used was made approximately $\frac{N}{3}$ in carbon tetrachloride. The oil was dissolved in carbon tetrachloride, and the bromine solution added, and water was floated on the solution. At the end of a definite period the excess of bromine was determined by the addition of an excess of potassium iodide and the liberated iodine titrated with sodium thiosulphate solution. The acidity of the water was also determined.

The total bromine absorbed was calculated from the thiosulphate titration, and the amount of bromine absorbed by the saturated hydrocarbons from the degree of acidity of the water. By deducting this latter amount from the total the real amount absorbed by the unsaturated hydrocarbons was obtained.

The table gives a comparison between the bromine values, calculated in terms of iodine for easy comparison, and Hübl iodine values.

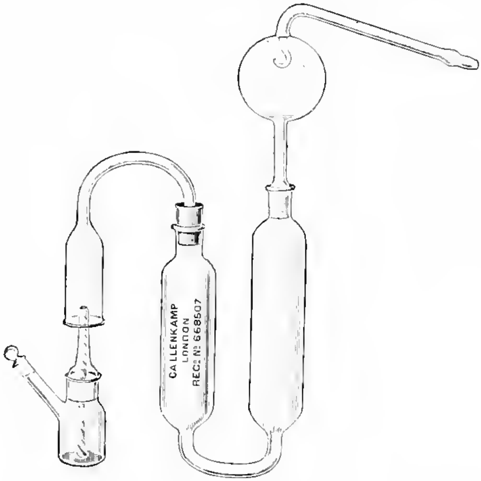
	Bromine Value as Iodine	Hübl
1	6·06	1·08
2	14·9	10·6
3	11·8	9·6
4	6·07	2·6
5	16·2	12·8
6	22·7	18·5
7	16·2	10·9
8	10·6	5·9

This work is being pursued further in the hope of reaching satisfactory conclusions.

CHAPTER VI

CHEMICAL TESTS (*Continued*)

Sulphur Determination.—Sulphur may be estimated by burning the oil in a lamp and absorbing the gases evolved in a suitable solvent. There are several modifications involving this principle, the merits of any one must be self-evident.



Esling's Apparatus.

Esling's modification is very simple in construction and operation. A determined weight of oil is burnt in the lamp, diluted with a suitable solvent, and the products of combustion are drawn through 20 c.c. $\frac{N}{16}Na_2CO_3$ solution contained in a U-tube, the second limb of which is filled with glass wool or glass beads. The size of the flame must be regulated to burn without the production of smoke; the rate at which the air is aspirated through the apparatus will largely govern this. When all the oil has been burned it is advisable to burn a little more of the solvent in the lamp to ensure the complete combustion of the oil. The sodium carbonate solution is carefully transferred to a beaker and the U-tube washed several times with distilled water, the washings being added to the solution, and then titrated with $\frac{N}{16}H_2SO_4$, using methyl orange as the indicator. The difference in the number of c.c.s between the volume of Na_2CO_3 and H_2SO_4 used gives directly the weight of sulphur expressed in milligrams which was contained in the oil.

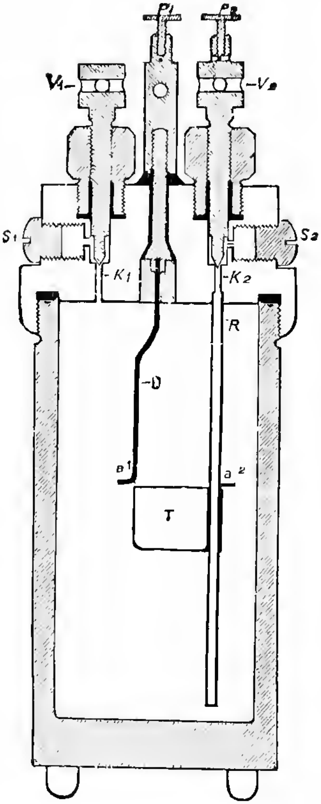
When using motor spirit, benzole, etc., dilute it with absolute alcohol; kerosene and lamp oils can be burned without a solvent, but lubricating oils should be diluted with amyl acetate.

The great advantage of this method over other methods is that large quantities of oil can be used if the sulphur content is low. The accuracy of the determination is of course dependent upon the efficiency of the absorption of the products of combustion of the sulphur compounds. Considerable trouble may be experienced in burning viscous oils. When making this determination the absence of acid fumes in the air is essential, and the products of combustion of coal gas, as coal gas contains sulphur compounds.

Burning the oil in a bomb, such as is used for the determination of the calorific value of fuels, leaves little to be desired from the point of view of accuracy.

The steel bomb is nickel-plated, has a lid to screw on firmly, and its capacity is about 300 c.c.; the lid is strengthened in the centre with a bridge through which pass the entrance and exit gas channels; the channel K2 with its continuation platinum tube R is for the introduction of oxygen, and channel K1 for the exit of the combustion gases; both channels are closed by means of screw spindles, V1 and V2, running in stuffing-boxes. If the atmospheric air is to be expelled from the autoclave the screw valve V1 must be opened for a moment when the oxygen is being introduced. This manipulation gives at the same time the certainty that the channels are not blocked. Close both lateral channels by means of screws S1 and S2. The platinum wire pole D passes through the centre of the lid, and this, as well as the platinum tube R, is fitted with a short collar A1, A2, round which the ignition wire is wound; T is the platinum or silica crucible or the clay cup; P1 and P2 are two small screw clamps for attaching to the electric circuit or wires. It may be pointed out that no great force is required in screwing on the lid ; care must be taken that both contact surfaces, that of the lead washer and that of the autoclave rim, are always kept free from grit, etc. The closing of the valves K1 and K2 requires, also, but moderate force; furthermore, the screw threads must be kept free from foreign matter, and it is advisable to smear a little vaseline on the screw threads and the contact surfaces of the valves.

The ignition wire should be thin, pure iron wire, coiled in the centre. The coil should be so arranged that it dips just into the oil. The pressure of oxygen inside the bomb must be between 25 and 30 atmospheres to ensure complete combustion. When performing this test it is well to remember that there have been cases when the top of the bomb has been blown off. To ignite the oil the two terminals on the lid of the bomb are connected to an electric circuit giving about 10 volts. About 1 grm. of oil is as much as can be used with safety. After combustion is complete, K1 is attached to a wash-bottle containing a solution of sodium carbonate, and V1 is slowly raised to allow the gases to escape through the wash-bottle. A current of air is finally drawn through the bomb after opening K2. The solution is boiled with a little bromine and the sulphate precipitated with barium chloride, after acidifying with hydrochloric acid, filtered, washed, ignited, and weighed. From the weight of precipitate the amount of sulphur can be calculated.



Bomb.

Comparative Tests on the Bomb and Lamp Methods

	Bomb	Lamp
Petrol . .	0·03%	0·03%
Kerosene A .	0·16	0·17
„ B .	0·22	0·204
Gas Oil A . .	1·66	1·65
„ B . .	1·29	1·30

according to Redwood.

In the hands of careful workers the sulphur may be estimated by allowing a known quantity of the oil to drop slowly into fuming nitric acid, and finally boiling the acid solution with successive small quantities of potassium permanganate. When the oxidation is complete the acid liquor is diluted with water, nearly neutralised, and the sulphur determined as barium sulphate.

Moisture.—The solubility of water in mineral oils is extremely small. Groschuff (*Zeit. f. Elektrochemie,* 17, 384, 1911) has found the following solubilities:

Temperature	Benzene	Kerosene
20° C.	0·061%	0·006%
50	0·161	0·024
94	—	0·097

and states that the solubility of water in transformer oil is about three to four times that of water in kerosene.

An oil may contain a considerable amount of water in suspension without its presence being detected by visual observation, but when the proportion of water exceeds a certain limit the oil appears cloudy; what this limit is it is difficult to say, because it appears to vary considerably with the same and different oils. It is highly probable that the dimensions of the water particles is one of the governing factors. It is worthy of note that mineral oils to which traces of aromatic compounds have been added do in some cases increase the limit to which water may be held in suspension without exhibiting opalescence. The discussion of emulsions of oil and water does not lie within the purview of this book as such emulsions are still undeveloped as lubricants.

The detection of very small quantities of water in oil is a very difficult proposition, and it is doubtful whether any method beyond a dielectric strength determination is in use. Even a dielectric strength determination does not necessarily indicate the relative proportion of water present.

Larger amounts of water can be detected by the restoration of the blue colour to anhydrous copper sulphate, or by heating the oil in a test-tube when, if water be present, crackling takes place. If the tube be held perfectly still in the flame appreciably small amounts of water can be detected through the condensation of the steam on the side of the tube, and further more distinct crackling is observed if the condensed water returns to the oil. This test is as good as it is simple. Another method which is claimed to be very sensitive is to heat a quantity of oil in a carefully dried distillation flask, fitted with a thermometer, to a temperature of 150° C., and maintain it at this temperature for at least thirty minutes. The presence of water is detected by the production of a blue colour on a test paper, suspended in the neck of the flask, made by dipping filter paper into a solution of ferrous ammonium sulphate, drying, and then dusting it with powdered potassium ferricyanide. The paper must be stored in a perfectly dry atmosphere. To arrest the entrance of moisture into the distillation flask during the test the side tube is attached to a tube filled with anhydrous calcium chloride.

The suggested method of rubbing the oil with eosin on a glass plate, and noting whether it becomes pink if water be present, might be applied to pale-coloured oils, but its application is essentially restricted.

The quantitative determination of water may be effected by distilling a quantity (100 c.c.) of the oil mixed with an equal amount of toluene or xylene and collecting 100 c.c. of the distillate in a graduated cylinder in which the volume of water can be seen. If the amount of water be small the distillate should be collected in a tube with a constricted end, to facilitate the accurate measurement of the water. This method of Marcusson is the standard one.

Davis (*Journ. Amer. Chem. Soc.*, 23, 1901, 487) prefers to dry in an oven at 100° C. a length of absorbent paper, such as is used in the Adam's method for fat determination in milk analysis, which is rolled loosely and secured by a cotton band. The dried coil of paper is weighed, uncoiled, and a quantity of the oil evenly distributed on it. It is then recoiled and secured by the same cotton band, reweighed to ascertain the weight of oil, dried at 100° C. and re-weighed. The loss in weight is due to the loss of water from the oil.

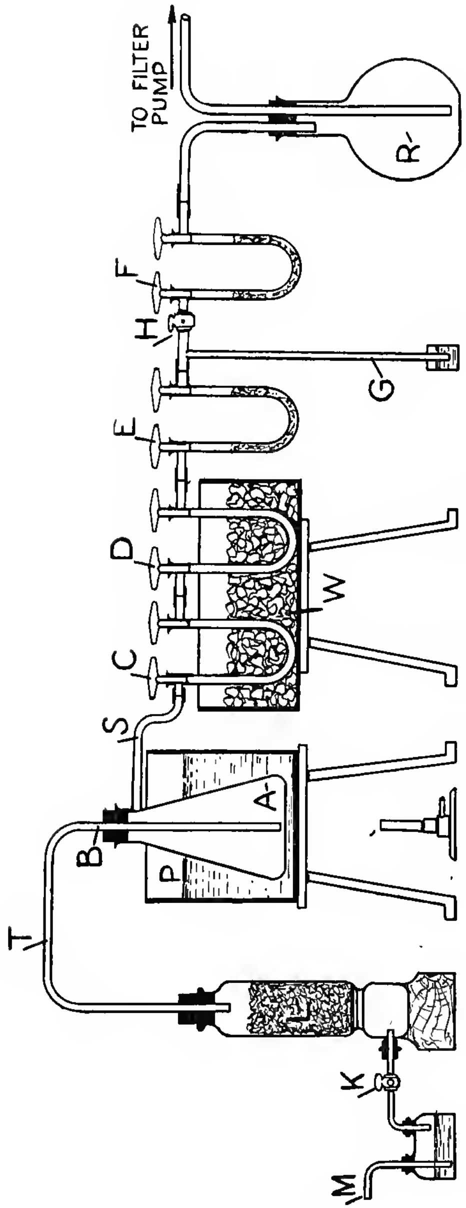
The measurement of the amount of acetylene evolved from a wet oil when treated with calcium carbide has not proved to be of great value in moisture estimations, neither has the method which involves the decomposition of the water with sodium and measuring the hydrogen evolved.

The extraction of water by glacial acetic acid is described by Shrewsbury (*Analyst*, 1914, 39, 529–531) as a rapid method. The turbidity temperature of the acetic acid with equal volumes of arachis and coco-nut oils is ascertained, then 10 c.c. of the standardised acid and 10 c.c. of the oil are shaken together, the acid layer separated, filtered, and 2 c.c. of the filtrate are heated with 2 c.c. of the standard oil until the mixture is clear and its turbidity temperature determined. Standards must be prepared by adding known quantities of water to the acetic acid. A correction is necessary for the effect on the turbidity temperature of non-aqueous substances in the oil; this is done by conducting a control determination on a dried sample of the oil. If the oil contains more than 2·5% of water more acetic acid must be used.

Rosenthal (*Chem. Zeit.*, 33, 1259, 1909) recommends diluting the oil with dry petrol and subjecting it to centrifugal action in a centrifuge developing at least 3000 r.p.m. Prior to measuring the separated water it is necessary to see that a false reading is not obtained through the admixture of dirt and other matter with the water. This test is used by the New York Produce Exchange. When using this test great care must be taken in obtaining specially strong glass vessels to withstand the stresses.

Philip (*Journ. Inst. Pet. Tech.*, 21, 1920, 43) claims to determine the amount of water to a considerable degree of accuracy. His method has been the target for much criticism, but whatever the criticisms may be the method must have wide application.

Two hundred grams of the oil weighed into a conical copper flask, A, which has a capacity of about 800 c.c. The flask is fitted with side tubes and is closed by an india-rubber bung, B,



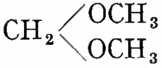
Apparatus for Moisture Determination.

through which a glass leading-in tube, T, passes to the bottom of the flask, its lower end being constricted to a fine orifice. The flask is immersed in a water-bath, P. The side tube of the flask is connected to an absorption train, which consists of the following: two small stoppered U-tubes, C and D, surrounded by a freezing mixture, W; two calcium chloride tubes, E and F, and a guard flask, R, which is connected to a pump. Between E and F a mercury pressure tube, G, is connected. The tube T is connected to a calcium chloride tower, L, and this to a tell-tale bottle, M. A tap, K, is interposed between M and L, and another, H, between E and F.

The tap K is closed and the pump started. When the mercury in G reaches a constant level H is closed. If the apparatus is air-tight, which it must be, the mercury will remain at the same level. Then air is drawn through at the rate of three bubbles per second, and the bath, P, raised to 212° F. The water from the oil is collected in C, D and E, and can be weighed in them. If any oil should pass over into C and D it can be separated and a correction made after weighing by absorbing the water with anhydrous copper sulphate and extracting the oil with dry petroleum spirit.

To avoid frothing of the oil dry pumice or anthracite should be placed in the flask with the oil, and a careful regulation of the reduced pressure may assist. In fact, the addition of pumice is always used as a precaution. The copper flask is used owing to the risk of fracture when removing the pumice.

Unsaturated Cyclic Hydrocarbons.—Nastjukoff (*Petrol.*, 4, 1336, 1397, 1909) has devised a method by which the unsaturated cyclic hydrocarbons can be determined in hydrocarbon oils by precipitating them with formaldehyde in the presence of sulphuric acid. The product so formed is called "formolit."

Heer (*Chem. Zeit.*, 35, 2245, 1911) claims that methylal  $CH_2\left\langle\begin{matrix}OCH_3\\OCH_3\end{matrix}\right.$ is preferable to formaldehyde inasmuch as it serves the dual purpose of a solvent and a condensing agent, and is more sensitive than formaldehyde towards aromatic hydrocarbons.

Marcusson (*Chem. Zeit.*, 35, 729, 1911) suggests the following method:

Twenty-seven grams of oil are dissolved in 50 c.c. of petrol in a 300 c.c. Erlenmeyer flask, and 30 c.c. of strong sulphuric acid carefully added without agitating the solution. The whole is then cooled in ice, and 15 c.c. of 40% formaldehyde added, and then the mixture is well shaken and allowed to stand in ice from about half an hour to one hour. The mixture is now poured into 200 c.c. of water at 0° C., ammonia is added in excess, and the precipitate filtered, washed with petrol, and then with cold water, and finally dried at 105° C. and weighed.

The oil which is freed from the unsaturated cyclic hydrocarbons may be recovered from the petrol filtrate. It is of a higher viscosity than the original oil, and usually of a lower specific gravity.

Richardson (*J. Ind. Eng. Chem.*, VIII, 319, 1916) claims that it is unnecessary to use formaldehyde, as exactly the same absorption takes place by using the sulphuric acid alone.

A valuable contribution to this test has been made to the Electrical Research Committee, but owing to it being part of a confidential report at the moment details must be withheld until it is passed for publication.

Paraffin.—The method adopted by the German Custom House authorities is based on the fact that paraffin is precipitated by alcohol from an ethereal solution of an oil containing paraffin wax.

One hundred grams of oil are rapidly distilled from a retort until all the oil which will distil below 300° C. has passed over, then the distillation is carried on until the oil in the retort cokes. The heavy distillate which collects above 300° C. is weighed. Of this distillate 5 to 10 grms. are treated with alcohol-ether (1 : 1) until all the oil has dissolved, and only paraffin remains undissolved. In distillates which are rich in paraffin it may be preferable to dissolve the oil in just sufficient ether, and then to add a quantity of alcohol equal in volume to the ether used. The mixture is then cooled to −20° C. and filtered, the paraffin washed with cooled alcohol-ether—unduly prolonged washing is to be avoided as the paraffin is slightly soluble in alcohol-ether—and then dissolved in hot benzene, or preferably alcohol if it be discoloured through contamination with resins, etc., and the solution evaporated to dryness in a tared dish, and weighed.

Owing to the solubility of the paraffin in alcohol-ether a correction must be made—0·2% is added when the distillate is completely soluble in alcohol-ether; 0·4% is added if the separated paraffin melts at 15° C., and 1% if the paraffin melts at a temperature above 15° C. In order to ascertain whether all the paraffin has been precipitated it is advisable to evaporate the filtrate, and redissolve in alcohol-ether (2 : 1), cool and filter as before.

References to this test: *Petrol.*, 4, 873 (1909); *Ding. Poly. Journ.*, 262, 473 (1886); *Chem. Zeit.*, 17, 1473 (1893).

A convenient form of apparatus for filtering at low temperatures has been designed by Eisenstein and Ziffer (*Chem. Zeit.*, 33, 1330, 1909).

Asphalt.—This substance may be regarded as a normal constituent in lubricating oils of the mineral oil class which may have had its genesis in the crude oil, or may have been formed during distillation. It appears to be in colloidal solution in the oil, and in such form it imparts a black colour to the oil; the degree of blackness may not, however, be taken as an index of the proportion of asphalt present. The mechanism of the reaction which results in the production of asphalt seems to be imperfectly understood, though it appears to be the resultant product, not necessarily the final product, of decomposition, oxidation, polymerisation, either severally or collectively. The changes under which the hydrocarbon goes may be initially invoked, and the velocity of the reaction accelerated by certain definite conditions, and under the influence of a number of widely differing substances whose influence may be direct or catalytic. Many difficulties in the isolation and estimation of the intermediate products in the transition of the hydrocarbon into asphalt must be surmounted before the chemistry of the change can be expounded. Asphalt is not a simple substance, but rather a mixture of substances, differing in composition, and governed by their mode of formation. Some asphalts are much lighter in colour than others; they differ in their melting-points, and differ in their solubilities in various solvents, hence it is that their estimation is so unsatisfactory. Methods have been proposed to differentiate between the differently occurring asphalts, but whether any of them solve the difficulty is open to doubt.

Nearly all mineral oils when in use in a machine yield asphalt, which is either precipitated or collects on some parts of the machine, in which form it is popularly known as "carbon." The so-called "carbon" does in some cases contain free carbon, but generally it consists mainly of asphalt, together with extraneous impurities, e.g. dust, sand, metallic particles, etc.

Oils containing natural asphalt—namely, the black oils—prove to be excellent lubricants for many purposes, provided the asphalt content is not excessive, and does not separate on the bearings and in the oil pipes, and thereby eliminate the risk of clogging which would inevitably ensue if the asphalt content were large. The maximum amount of asphalt which is permissible in a lubricating oil must essentially vary according to the purpose for which the oil is to be used. An oil which is intended for lubricating points on a railway, or carriage axles, may be richer in asphalt than an oil which is to lubricate the bearings of a locomotive.

Asphalt is frequently determined by thoroughly mixing 100 c.c. of oil with 300 c.c. of petrol, and allowing the mixture to stand twenty-four hours, then the petrol is decanted off, and the precipitated asphalt collected on a filter paper, washed with petrol, dried at a temperature not exceeding 60° C., treated with hot benzene to separate any material which may have been precipitated with the asphalt, filtered, and the filtrate evaporated in a tared dish, and weighed. If the asphalt be dried on a filter paper at a temperature above 60° C. it sometimes melts and adheres tenaciously to the paper when it cools, and it is then difficultly soluble in benzene.

The amount of asphalt precipitated by hydrocarbons of low boiling-point is greater the lower the boiling-point of the hydrocarbons used; but since the amount of asphalt precipitated by hydrocarbons of low boiling-point from most lubricating oils is very small an inexpensive precipitant, such as commercial petrol which has been redistilled, and the fraction passing over up to 110° C., can be used instead of the more expensive hexane or petroleum ether.

A more tedious, but more stringent, method consists in dissolving a known quantity of oil in a large excess of ether and then adding slowly, with constant stirring, a quantity of 96% alcohol equal to half the volume of ether added. The mixture is allowed to stand at least six hours, and then filtered, and washed with a mixture of alcohol and ether mixed in the proportion 1 : 2. The residue is dissolved in hot benzene as before and weighed. If any wax is present the residue should be extracted with absolute alcohol.

Ramsbottom made some tests in connection with the Mineral Oil Panel of the British Engineering Standards Association, 1920, to see if the petroleum spirit (B.P. below 40° C.) gave very different results from distillates of higher boiling range.

Precipitant	Asphaltic Matter
Petroleum Spirit (B.P. below 40° C.)	2·3%
Shell A	1·16
Distillate I (B.P. 46°–52° C.) .	2·03
,, II (B.P. 64°–83·5° C.) . contains 9% benzene	1·25
,, III (B.P. 95°–100° C.) . contains 8% aromatics	0·82
,, IV (B.P. 109°–113° C.) . contains 9% toluene	0·84

The distillates were obtained from Shell A.

In order to throw light on the behaviour of the different classes of hydrocarbons present in petrol, solubility experiments were carried out on asphalt precipitated from mineral oil by petroleum spirit (B.P. below 40° C.).

Solvent	Percentage extracted	Grms. per litre at 15° C.
Cyclohexane . . 80% pure	95%	2·4
Shell A distillate B.P. 60°–80° C. . . contains 13% benzene	30	0·75

The amylene fraction from cracked spirit dissolves asphaltic matter quite readily.

Thus it would appear as if the precipitant should consist of the saturated hydrocarbons of the methane series.

Various methods have been proposed to ascertain the liability of lubricating oils to " gum," and form deposits.

Carbon Residue Test. Gray's Method.—In a silica distillation flask having a bulb $1\frac{3}{4}$ in. in diameter and neck $\frac{9}{16}$ in. internal diameter, and 4 in. long with a side tube $5\frac{1}{4}$ in. in length and $\frac{3}{16}$ in. bore, the side tube being set 1 in. above the top of the bulb, is weighed 25 c.c. of the oil. The neck of the flask should be closed with a good-fitting cork, and the neck wrapped with asbestos cord as far as the side tube. The flask is fitted to an air condenser by an asbestos plug. The oil is heated at such a rate that the first drop falls from the condenser in five minutes, and every succeeding drop at the rate of one drop per second. Care must be exercised, by avoiding draughts and unequal heating, to prevent condensed vapours from returning to the flask. When all the oil has distilled heat the residue for five minutes, and burn off the carbon from the neck of the flask above the side tube, then allow the flask to cool, and weigh.

By this method it is stated that motor oils of medium viscosity should give not more than 0·5% of carbon residue, and high viscosity motor oils 1·25%. In comparing oils by this method consideration should always be given to the fact that high viscosity oils give a greater carbon residue than do low viscosity oils.

Gumming Test.—Gill (*Journ. Am. Chem. Soc.*, 24, 1902, 467). This test is claimed to be a measure of the degree of carbonisation that an oil will give when used in an internal combustion engine. To 5 grms. of oil are added 11 grms. of nitrosulphuric acid whilst the oil is shaken thoroughly, and cooled in water to keep its temperature below 15° C. Brown spots develop, or in the case of bad oils dark-coloured masses form around the edges of the oil, and become red in two hours. Then add three successive portions of 70° to 80° naphtha to dissolve the oil, allowing time for complete separation before decanting the naphtha solution. The acid can be neutralised with ammonia. The tar can be collected on a filter, finally washed with gasoline, dried, and weighed. The quality of the oil is judged by the low tar yield. This test is of little value.

A number of direct oxidation tests on mineral oils were conducted by Dr. Fox and the author in connection with the Mineral Oil Panel of the British Engineering Standards Association in 1920. Fox half filled a tube $6\frac{1}{2}$ in. × $1\frac{1}{4}$ in. with the oil to be tested and placed it in an oil-bath maintained at a temperature of 150° C. Air was blown into the tube at such a rate that 2·5 cu. ft. passed through the oil during the test, which occupied eighteen hours. The oil was subsequently diluted with twelve volumes of petroleum spirit (B.P. 40° to

60° C.), allowed to settle, filtered and washed. The residue was dissolved in hot benzene, and the extract evaporated to dryness and weighed. The results obtained were

A	0·108%
B	0·032
C	0·067

The author used the standard sludge test for transformer oil (*vide* p. 88), and obtained the following results :

A	0·3%
B	0·033
C	0·2
D	0·05
E	0·2

The oils were heated in an open dish, placed in an air oven at 250° C. for three hours, and the matter insoluble in petroleum spirit determined—

A	0·12%
B	0·075
C	0·11

The **coke value** was instituted as a guide to the carbonising propensities of an oil when used in an internal combustion engine, based upon the assumption that the carbon produced was due to the burning of the oil on the cylinder wall.

Five grams of oil are gently warmed in a platinum dish until it ignites. The flame of the burning oil should not exceed 4 in. When the flame dies out, remove the burner and weigh the residue. Residue expressed as percentage of oil used gives the coke value.

COKE VALUE OF OILS USED IN OXIDATION TESTS

A	0·70%
D	0·89
E	0·80

From engine trials it has been found that B and D are superior oils to A and E. As this superiority is revealed in the oxidation tests and not in the coke value tests, it is reasonably certain that the coke value and similarly obtained values are unreliable.

Ramsbottom has compared several well-known methods for determining the coke value for the Aircraft Sub-Committee on Chemicals of the British Engineering Standards Association, of which the author is a member, and has found them to be unreliable. He has recently devised a new method, which appears to give consistent results with different workers.

A glass or silica tube 1 in. in diameter and $\frac{3}{64}$ in. thickness of wall, shall be drawn out at one end to a capillary of $\frac{1}{16}$ in. diameter and $\frac{3}{8}$ in. in length, so that the length of the bulb from the base to the shoulder shall be $1\frac{1}{2}$ in. and from the base to the tip of the capillary about $2\frac{1}{4}$ in. The bulb shall be weighed, and about 5 grms. of oil introduced. The bulb shall then be placed in an iron sheath, closed at one end, 3 in. long, 1 in. internal diameter, the thickness of the wall $\frac{1}{32}$ in. The sheath and enclosed bulb shall then be placed in a bath of molten lead at a temperature of 550° C. The heating shall be continued until fumes cease to be evolved. The bulb when cool shall be weighed.

Artificial Thickners.—To impart an abnormal viscosity to an oil various substances are occasionally used, amongst which may be mentioned sodium, potassium, calcium, and aluminium soaps, and caoutchouc. The thickners may be added for some very definite purpose, but generally they may be considered to be either adulterants or impurities.

Soaps may be detected by boiling the oil with water to which phenolphthalein has been added. Their presence might be indicated by the development of a pink coloration. Schweitzer and Lungwitz (*Journ. Soc. Chem. Inst.*, 13, 1178, 1894) dissolve 5 to 10 c.c. of oil in 5 c.c. of ether, and add a few drops of metaphosphoric acid solution, shake and allow to stand. A flocculent precipitate of a metaphosphate indicates the presence of a soap. The most reliable method is to determine the amount of ash in the oil.

Caoutchouc is precipitated as a flocculent mass by dissolving the oil in four parts of ether and adding three parts of alcohol.

Transformer Oil.—The subject of transformer oil has probably demanded more attention during the past few years than any other mineral oil, and strange it is that the work which has been done has been confined to a few workers, with but a few exceptions. The use of mineral oil for electrical insulating purposes is often believed to date back to 1906, when Moody was granted a patent, but the author is of the opinion that it was used before this date. Digby and Mellis, in 1910, read a paper before the Institution of Electrical Engineers defending the use of mineral oil for electrical insulating purposes, and in 1910 Duckham (*Electrical Times*, January 20th) made suggestions as to the cause of the formation of solid deposits which occur in transformers when mineral oil is used. Michie studied these deposits very closely and devised a test to ascertain the liability of a mineral oil to deposit sludge when used in a transformer, and published a short paper in the *Journal* of the Institution of Electrical Engineers in 1913. The subject-matter of that paper has been taken as the theme for much of the work which has since been done on transformer oils. Later, in 1913, the Research Committee of the Institution of Electrical Engineers formed a sub-committee to organise research on this subject. Digby issued a report (*J.I.E.E.*, 53, 239, 1915) on the findings of this committee; a further report was made in the same journal in April, 1916. Subsequently this small sub-committee was transferred to the Electrical Research Committee, which has Government recognition, who formed the Insulating Oil Committee which now deals with the whole subject. The author is a member of that committee. This committee has conducted a considerable amount of research, on which a report will be published in due course. At the present moment, however, these reports are confidential, mainly because the subject which involves the combined efforts of chemist, physicist, and engineer requires careful dovetailing, and until this is complete it is undesirable to publish any one report.

The sludge test which was designed by Michie, and standardised in detail by the committee, is in use in several laboratories, and, therefore, should be described.

Method of Test.—One hundred c.c. of the oil are introduced into a clean, dry, round-bottomed flask which fits by means of a ground-in joint to an all-glass condenser having the shape and dimensions given in Figure 1. A piece of pure sheet copper, having a bright planished surface and measuring 2 in. × $1\frac{1}{4}$ in. × 0·004 in. thick, is rolled round sufficiently to slide easily down the neck of the flask, and is so bent that when introduced into the flask the edges spring apart leaving an opening about ¼ in. wide.

The coiled strip stands vertically in the bottom of the flask. The whole of the bulb of the flask is immersed in an oil-bath, care being taken that when the oil-bath reaches 100° C. the ground joint is above the surface of the oil, in order to ensure that no leakage of the latter into the test flask can occur.

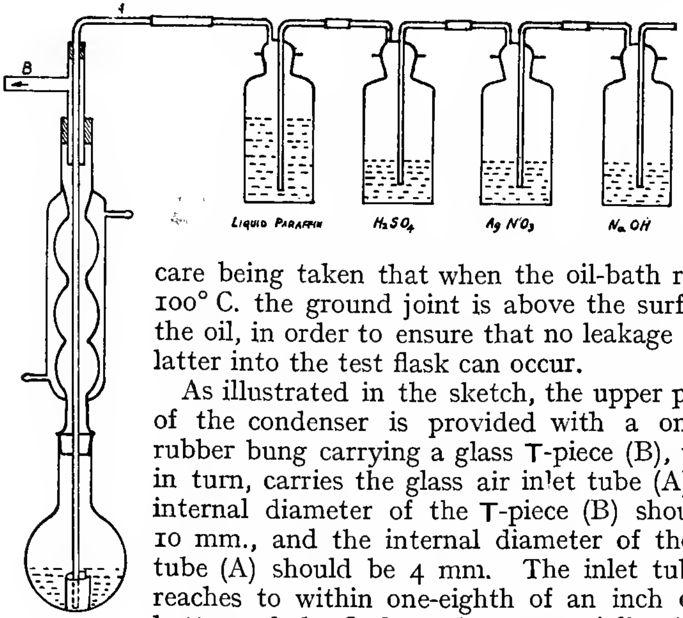


Fig. 1.

As illustrated in the sketch, the upper portion of the condenser is provided with a one-hole rubber bung carrying a glass T-piece (B), which, in turn, carries the glass air inlet tube (A) ; the internal diameter of the T-piece (B) should be 10 mm., and the internal diameter of the inlet tube (A) should be 4 mm. The inlet tube (A) reaches to within one-eighth of an inch of the bottom of the flask, and passes axially through the cylinder of copper. By means of a pump, fan, or aspirator, suction is applied to the tube (B) so as to cause a current of air to be drawn through (A), and bubble through the oil.

The air before entering the tube (A) is dried and purified by passing it through three wash-bottles containing sodium hydrate solution, specific gravity 1·355, 10 % silver nitrate solution and concentrated sulphuric acid respectively.

The inlet tubes of the wash-bottles should dip ½ in. below the surface of the reagents. The rate at which air is bubbled through the oil is 0·07 cu. ft. per hour, and is indicated by means of a tell-tale bottle (F) inserted between the sulphuric acid wash-bottle and the inlet tube (A).

The inlet tube of the tell-tale bottle has an internal diameter of 4 mm. and dips 2 in. below the surface of the liquid in the bottle (F), which should be half filled with liquid paraffin (B.P. sp. gr. 0·8).

The temperature of the oil-bath containing the test flask is maintained at a constant temperature of 150° C. for forty-five hours, and during the period of heating the current of air is adjusted so as to pass through the tell-tale tube at the rate of three bubbles a second. The rate should be checked from time to time by means of an accurate gas-meter and should conform to 0·07 cu. ft. per hour measured at Normal Temperature and Pressure.

After the forty-five hours' treatment the flask is removed from the oil-bath, allowed to cool, the contents transferred to a beaker, care being taken to remove all the deposit ; diluted with three times its volume of petroleum spirit, and allowed to stand for twelve hours for the sludge to separate.

The petroleum spirit used should have a specific gravity of 0·70 to 0·72 at 15·5° C., and not less than 75% by volume should distil below 110° C.

The liquid is then decanted through a No. 40 Whatman filter paper, the filter paper washed free from oil by means of petrol spirit, and the deposit then washed on to the filter paper by means of petrol spirit. The deposit on the filter paper is then thoroughly washed with petrol spirit until free from oil, and dried at 100° C.

In the event of the deposit being large it should then be detached from the filter paper, crushed and re-dried at 100° C. and then re-weighed. Any traces of deposit which adhere to the paper should be removed by means of hot benzol or other suitable solvent; the solvent is then evaporated off and the residue weighed.

When only a small amount of deposit is obtained the whole is treated with solvent, as above.

The result is expressed as a percentage, thus :

$$\%\ \text{Sludge} = \frac{\text{Weight of deposit in grams}}{\text{Specific gravity of the oil}}$$

This test, whilst being extremely useful, and probably the best yet designed for its purpose, is not clearly understood. That it is an oxidation test is certain, but what it is in the oil which oxidises is not certain. The unsaturated hydrocarbons in the oil are generally regarded as the progenitors of the sludge; in some measure this may be true, but the author has found that by treating oil with chlorine, hypochlorous acid, and extracting the resultant bodies, no appreciable diminution in sludge has resulted, nor after treatment with potassium permanganate with sodium hydroxide or with dilute sulphuric acid. By such treatment the unsaturated bodies, in some measure at least, should be removed. If they are then there is some evidence to dispel this idea. Efforts to polymerise the oil with aluminium chloride, to reduce the sludge value, have given negative results. Picric acid was considered a possible reagent to remove sludging constituents, but it was found to be valueless. The application of liquid sulphur dioxide to separate the sludging constituents appeared to be a hopeful solution to the problem; this also failed, although there was some reduction after repeated extractions, but it was insufficient to warrant any hopeful conclusions.

Radcliffe (*J.S.C.I.*, 1916, XXXV, 341) has adopted the current belief that iodine value and sludge value are related, or in other words that the sludge value and the unsaturated hydrocarbon content bear some connection to each other.

No.	Sp. Gr.	Sludge	Hübl	Wij's
1	0·8582	0·7	14·5	29·3
2	0·8848	0·1	1·7	7·7
3	0·8441	0·05	1·7	6·1
AB 2	0·8714	0·4	0·4	21·6
AB 9	0·8588	0·1	12·7	27·5

The author has compared the same values.

No.	Sludge	Hübl
1	Nil	1·08
2	0·35	10·6
3	0·35	9·6
4	0·36	2·6
5	0·35	12·8
6	0·6	18·5
7	0·7	10·9
8	0·7	5·9
9	0·7	15·5
10	0·8	13·8
11	0·9	12·8
12	1·2	13·9

In the author's opinion these figures do not exhibit any close relationship, or even agreement. The fact that the oil which gives the least sludge gives the lowest iodine value may be, and probably is, due to its particular mode of manufacture. At the present moment it would be a bold assumption to state that the sludging qualities of an oil can be measured by its iodine value.

The colour has been taken as a criterion of the liability of an oil to sludge. This belief is entirely misleading, for a white oil may give no sludge or it may give much; on the other hand, a dark amber-coloured oil may give less sludge than a pale amber oil, or even a white oil. Considerable difficulty is experienced in describing the exact colour of an oil; nevertheless, the following table may convey some idea of the want of relationship between colour and sludge value.

No.	Colour	Sludge Value
1	White	Nil
2	Red	0·35%
3	Almost white	0·35
4	Very pale	0·36
5	Pale coffee	0·35
6	Shade darker than 5 . .	0·6
7	,, ,, ,, 6 . .	0·7
8	,, lighter ,, 4 . .	0·7
9	,, ,, ,, 5 . .	0·7
10	,, between 5 and 6 .	0·8
11	,, identical with 5 .	0·9
12	,, ,, ,, 5 .	1·2

CHAPTER VII

OXIDATION OF PETROLEUM

Production of Asphalt by the Oxidation of Petroleum.—The production of asphalt from petroleum is of peculiar importance to users of lubricating oil, and transformer oil. It is to the formation of asphalt deposits that one looks for the greatest source of trouble in the lubrication of steam cylinders, steam turbines, and internal combustion engines; also the deposits found in oil-cooled transformers are generally composed of oxidation products of petroleum.

The first reference to the production of asphalt from petroleum appears to have been made by Jenney (*Am. Chemist.* 5, 1875, 359). He found that by passing a current of oxygen through petroleum oxidation occurred, resulting in the formation of a solid deposit, which resembled natural asphalt. The velocity and extent of the reaction could be increased by the addition of litharge or potassium to the oil, also by raising the temperature of the oil. Further investigation led him to the discovery that when petroleum is treated with sulphuric acid, the acid layer separated, diluted with water, the oily layer which rises separated, and then heated, and blown with air asphalt is rapidly produced. This discovery was protected by U.S.A. Patent 178061 (1876).

The researches of Ostrejko throw a considerable amount of light upon the decomposition of petroleum. Working with Baku petroleum, he found that when petroleum is exposed to sunlight in the presence of air it develops acidity, and produces a precipitate. If, however, the experiment be conducted in the dark the amount of oxidation is practically nil. The absorption of air is greatly influenced by the degree and method of refinement of the petroleum.

As one might expect, heat is a determining factor in the oxidation of petroleum. Schreiber (*Z. angew. Chem.*, 23, 1910, 99) found that the amount of asphalt produced is dependent upon the temperature to which the oil is heated. Waters (*Journ. Ind. Eng. Chem.*, 3, 1911, 233) obtained similar results, but he found that the temperature of the oil, the period of heating, the free access of air, are not the only factors which must be governed to obtain quantitative results. Michie (*Journ. Inst. Elec. Eng.*, 51, 1913) found that the deposits in oil-cooled electrical transformers are simply oxidation products of petroleum. His investigations show that the rate of oxidation is influenced by certain metals with which the oil may be in contact, and by the degree of purification of the oil. He was unable to cause the oil to deposit any precipitate merely by an electrical stress, neither was Meyerheim (*Chem. Rev. Fett-Harz-Ind.*, 19, 1912, 28) able to increase oxidation by radium rays nor by the mercury lamp. Zaloziecki and Zielinski (*Orig. Com. Eighth Inter. Cong. App. Chem.*, 10, 335) have shown that petroleum is susceptible to increased oxidation when treated with various reagents, such as ferric chloride, aluminium chloride, zinc chloride, phosphorous pentoxide, etc. Other reagents—sodium carbonate, phosphorus, sodium, barium peroxide—are without action under similar conditions. Stolzenberg (*Chem. Rev.*, 13, 1906, 54, 79) believes that the formation of deposits in steam cylinders is usually traceable to the methods of operation of the engine, and not to impurities in the oil. He has adduced evidence that flue-dust, iron oxide, etc., get into the cylinder and become governing factors in the formation of deposits. This statement could be interpreted as meaning that any oil of suitable viscosity and flash-point belonging to the mineral class can be used in a steam cylinder without fear of deposits forming, provided that the design of the engine is such as to exclude the possibility of the entrance of flue-dust, etc., into the cylinder. This of course is not correct, for as every engineer knows some oils give rise to more deposit than others when used under similar conditions. It is an indisputable fact, however, that until the engineer realises that oils are not inert bodies, and designs his engine with this fact in mind, deposits to a more or less degree will continue to give inconvenience, although he may rest assured that the manufacturer of lubricants is endeavouring to discover a non-carbonising lubricant. The author has found that certain oils do not carbonise when heated with steam at as high a temperature as 1000° F. and pressure of 200 lb. per sq. in. for a prolonged period, but in the presence of flue-dust, etc., some carbonisation was found. The conditions of the experiments were made to resemble the conditions occurring in a steam cylinder working at given temperatures and pressures, and different rates of oil feed. Southcombe (*J.S.C.I.*, 27, 1908, 308) has also shown that iron oxide is largely responsible for the formation of deposits in steam cylinders, but he does not venture to suggest that the oil is of secondary importance in the formation of these deposits.

The mechanism of the reaction which results in the formation of asphalt is but very imperfectly understood; we do know that it is not a simple reaction, and that it probably takes place in several stages, also that several substances, and varied conditions, can accelerate the transformation of petroleum into asphalt. It is even doubtful whether those substances which accelerate the formation of asphalt act as catalysts, or act chemically. From experiments conducted in the author's laboratory it would appear that certain substances react catalytically, whilst others react chemically, at least to a certain stage in the reaction. The deposits from steam cylinders nearly always contain iron oxide, or flue-dust, sometimes in appreciable quantity. Samples have been examined by the author in which it has been found that the deposit consisted of laminations, each of which contained different amounts of foreign matter, and that the foreign matter acts as a nucleus for the formation of the deposit. If this be so, then it appears that the decomposition of the oil takes place when the steam is shut off from the cylinder. It is then that a vacuum is created within the cylinder and flue-dust and flue-gases are drawn in. The hot oil on the piston and cylinder wall becomes mixed with the dust and oxidation ensues. It is possible also that the sudden change from a high pressure to a low pressure may have some influence upon the decomposition of the oil.

The influence of sulphur and sulphur compounds upon mineral oils still gives rise to conflicting views. Gallety (*Chem. News*, 24, 1871, 162) found that hydrogen sulphide is evolved when sulphur is heated with paraffin; also Lidoff (*Chem. Zentr.*, 1882, 22) made hydrogen sulphide by adding "naphtha" to sulphur heated to 350° C. to 400° C. In 1892 Dubbs patented a process in the U.S.A. for manufacturing asphalt by heating heavy oils with sulphur. Willstaetter and Sonnenfeld (*Ber.*, 47, 1914, 2801) have shown that oxidation of olefines rapidly takes place by air in the presence of phosphorus, but under similar conditions sulphur had no action. At elevated temperatures, however, sulphur accelerates oxidation of the olefines. Brooks and Humphrey (*Journ. Ind. Eng. Chem.*, 1917, 746) find that oxidation of petroleum is noticeable in the presence of mercaptans and sulphides at atmospheric temperatures, and at higher temperatures asphalts are produced by the action of sulphur on mineral oils. They believe that oxidation is essential to produce the polymerisation of the petroleum into asphalt. Engler and Zaloziecki conclude that polymerisation is the main factor in the formation of asphalt. Staudinger's (*Chem. Ztg.* (1912), 1188; (1913) 379) experiments prove that a very small amount of air has a very marked action in effecting polymerisation of certain unsaturated hydrocarbons.

In view of the interest which has been manifested in the composition of the deposit which forms in transformers and steam turbines, and the resultant products from its fractional distillation reference to a paper by Bergman (*Zeit. ang. Chem.*, 1918, 31, 69–70) is worthy of mention. He passed air through paraffin wax, which had been highly refined, for eighteen days at 135° C., and fractionally distilled the resultant soft brown product. Formic, acetic, and butyric acids were collected, also lignoceric, and probably isopalmitic acids.

CHAPTER VIII

OLEOGRAPHY

OLEOGRAPHY was introduced many years ago by Professor Tomlinson to exhibit the differences produced by films of essential oils. Later Moffat (*Chem. News*, XVIII, 299) adopted Tomlinson's idea for the identification of oils and to detect sophistication of them. The oleograph test consists in placing a drop of oil on a perfectly clean surface of water, and noting the configuration of the film produced. Each oil produces a design peculiar to itself under definite conditions, hence any oil can be identified by noting the design produced when a drop of the oil is placed on water. A record of the design can be obtained by placing a piece of filter paper upon the oil film on the water, and then transferring it to the surface of diluted ink, when the non-oily portion will be stained, leaving the film design in white relief.

The scheme is never practised now, but whether with our increasing knowledge of oil films it will ever be revived and improved remains to be seen. The spreading of a film of one substance on another, especially water, has received a considerable amount of attention; in fact, the factors which cause a substance to spread are fairly well understood, but the analyst does not seem to have interested himself in this direction, for one would think, as Tomlinson did, that the formation of films might be of value if only as a rapid qualitative test.

Lord Rayleigh (*Phil. Trans.*, 48, 331, 1899) believed that when an oil spreads on water without hindrance it spreads until it has assumed a layer one molecule in depth. He found the thickness of a film of castor oil to be $1{\cdot}3 \times 10^{-7}$ cm., and olive oil to be $1{\cdot}0 \times 10^{-7}$ cm. Devaux has published a number of papers dealing with oil films, a review of which will be found in the *Annual Report of the Smithsonian Institute* for 1913. The method adopted by Devaux to determine the thickness of the film was to drop a solution (1 : 1000) of the oil in benzene on to water. The benzene evaporated, leaving a film of oil on the surface of the water. From the volume of oil used and the area covered by it he calculated the thickness of the film. For triolein he obtained a value of $1 \cdot 1 \times 10^{-7}$ cm. The theoretical value, he states, should be $1 \cdot 13 \times 10^{-7}$ cm., calculated from Perrin's value for the Avogadro's constant, its molecular weight, and density. Labrouste (*Compt. rend.*, 158, 627, 1914) has extended the subject, using palmitic and stearic acids, myristin, laurin, palmitin, cetyl alcohol, etc. According to Langmuir (*Journ. Am. Chem. Soc.*, XXXIX, 1863, 1917) the spreading is due to an attraction between the group molecules of the oil and those of the water. The water attracts a portion of the oil molecule, and the remainder of the molecule is attracted by the other oil molecules. Oleic acid, for example, spreads by virtue of the carboxyl group being dissolved in the water, and the hydrocarbon chains arrange themselves vertically above the carboxyl group, the upper surface thus consisting of methyl groups. From this theory hydrocarbons should not spread, a fact which was shown to be the case by Hardy (*Proc. Roy. Soc.*, 86A, 610, 1912).

Langmuir (*Met. Chem. Eng.*, 15, 469, 1916) proposed to explain surface tension (or surface energy) by considering the structure of the surface layer of atoms in the molecule of the substance. The least active portions of the molecule arrange themselves on the surface, whereas the more active portions are drawn downwards. The active portion is described as being characterised by a strong stray field (residual valence), hence the surface energy is merely a measure of the potential energy of the electromagnetic stray field which extends out from the surface layer of atoms.

The surface tension of all the hydrocarbons of the C_nH_{2n+2} series, from hexane to molten paraffin, have the same value, namely, 46 to 48 ergs per sq. cm. In the light of this theory it is easy to understand this if the surface layer be composed of the methyl groups. Further, the surface tensions of methyl alcohol, ethyl alcohol, etc., are almost the same as those of the paraffins, hence the same explanation is applicable.

In the case of benzene it is assumed that the ring lies flat, its surface tension being 65 ergs per sq. cm., but when an active group, such as hydroxyl, is introduced the surface tension rises to 75 ergs per sq. cm., due to the tilting of the ring. Similarly, any other active group which is sufficiently powerful to tilt the ring will raise the surface tension to 75. Two active groups in the ortho position have no greater influence than one, but if they be in the para position the surface tension becomes about 85.

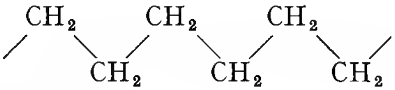
Substance	Formula	Cross Section Sq. cm.	$\sqrt{\text{Cross Section}}$ Cm.	Length Cm.	Length per carbon atom
Palmitic acid . .	$C_{15}H_{31}$ COOH	21×10^{-16}	$4·6\times10^{-8}$	$24·0\times10^{-8}$	$1·5\times10^{-8}$
Stearic acid . .	$C_{17}H_{35}$ COOH	22×10^{-16}	$4·7\times10^{-8}$	$25·0\times10^{-8}$	$1·39\times10^{-8}$
Cerotic acid . .	$C_{25}H_{51}$ COOH	25×10^{-16}	$5·0\times10^{-8}$	$31·0\times10^{-8}$	$1·20\times10^{-8}$
Tristearin . . .	$(C_{18}H_{35}O_2)_3$ C_3H_5	66×10^{-16}	$8·1\times10^{-8}$	$25·0\times10^{-8}$	$1·32\times10^{-8}$
Oleic acid . . .	$C_{17}H_{33}$ COOH	45×10^{-16}	$6·8\times10^{-8}$	$11·2\times10^{-8}$	$0·62\times10^{-8}$
Triolein . . .	$(C_{18}H_{33}O_2)_3$ C_3H_5	126×10^{-16}	$11·2\times10^{-8}$	$13·0\times10^{-8}$	$0·69\times10^{-8}$
Trielaidin . . .	$(C_{18}H_{33}O_2)_3$ C_3H_5	120×10^{-16}	$11·0\times10^{-8}$	$13·6\times10^{-8}$	$0·72\times10^{-8}$
Cetyl palmitate .	$C_{15}H_{31}COO$ $C_{16}H_{33}$	23×10^{-16}	$4·8\times10^{-8}$	$41·0\times10^{-8}$	$2·56\times10^{-8}$
Myricyl alcohol .	$C_{30}H_{61}$ OH	27×10^{-16}	5.2×10^{-8}	$41·0\times10^{-8}$	$1·37\times10^{-8}$

Hardy lends some support to Langmuir in his deduction that great chemical stability of the paraffin makes chemical interaction with water impossible. Some degree of chemical action would seem to be necessary to make one fluid spread as a film between two others (air and water).

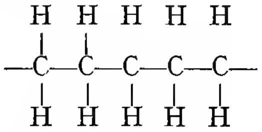
Langmuir, working on similar lines to Marcelin (*Ann. Phys.*, 1, 19, 1914), obtained some very interesting data of films on water.

The molecule of tristearin has the same length as stearic acid, but three times the cross-section. Thus each of the three active groups have been drawn down to the surface of the water while the hydrocarbon chains are packed side by side, and are erect upon the surface, just as is demanded by the theory.

The length of the molecule of cetyl palmitate is nearly double that of palmitic acid, whilst the cross-section is nearly the same. From this fact it would appear as if the molecule were arranged vertically with the carboxyl group in the middle and having a methyl group at each end; but this is contrary to the theory, hence it must be assumed that the carboxyl group is at the base of the molecule, and the two hydrocarbon chains placed vertically above it. The difference in the cross-section of the molecules of palmitic acid and cetyl alcohol might be explained by imagining that the chains are arranged somewhat as follows:



in palmitic acid, and as



$$\begin{array}{ccccccccccc} & H & & H & & H & & H & & H & \\ & | & & | & & & & & & & \\ - & C & - & C & - & C & - & C & - & C & - \\ & | & & | & & | & & | & & | & \\ & H & & H & & H & & H & & H & \end{array}$$

in cetyl alcohol.

This assumption finds some support in the length per carbon atom, as given in the table.

It appears to the writer that the orientation of the atoms in cetyl palmitate offers a very possible explanation of the peculiar value of sperm oil as a lubricant. It certainly dissipates the idea that sperm oil owes its great lubricating value to the smallness of its molecules. A molecule arranged in this fashion should be capable of withstanding great pressure, for in a given area there is a large number of pillars of oil of considerable length, each pillar being a single molecule which consists of two attached pillars. Supposing the pressure were sufficiently great to distort the molecule it would be flattened to form a film of considerable area, and therefore cover a large area of the lubricated surface, thus preventing in great measure the contact of metal surfaces.

CHAPTER IX

SELECTION OF LUBRICANTS

Selection of Lubricants.—Nearly all the various chemical, physical, and mechanical tests which have been suggested to assist in the selection of a lubricant for a specific purpose leave much to be desired, and are generally valueless to the chemist and engineer whose knowledge of lubricants in general, under working conditions, is limited. Such tests, however, may be indicative, but they cannot be considered in any way as absolute. The only known reliable method of testing a lubricant is to subject it to the conditions under which it is to work in actual practice, and to watch its behaviour carefully for a prolonged period. A test of short duration, and one which is not kept under careful observation, may be very misleading; further, such a test may yield results which are exactly the reverse from what would occur when the oil is used for a longer period. This point cannot be too strongly emphasized. The laboratory tests are of value in differentiating between various oils, and when considered in conjunction with the results of similar oils working under conditions similar to those under which the new lubricant is proposed to work. Lubricating oils sometimes give anomalous results when used upon entirely new engines, and when following another oil which has not been thoroughly removed from the engine.

The first point to be considered when selecting a lubricant for a specific purpose is whether it shall be a pure mineral oil, a fatty oil, a compound oil, or a lubricant of a special character. Having decided this it becomes necessary to decide upon the nature of the mineral oil, of the fatty oil, in the case of a compound oil of the mineral oil and the fatty oil respectively, or upon the characteristics of the constituents of a special lubricant, and the relative amounts of the various oils in the lubricant. For certain classes of work a unanimous opinion exists as to what type of lubricant shall be used, but for other classes of work divided opinion is to be met. It is highly probable that differences of opinion will always exist as long as machines are under the influence of the idiosyncrasies of human nature. The efficient working of any machine is largely governed by the skill and attention given to that machine by the engineer. Too much or too little oil may be given, resulting in excessive carbonisation or emulsification, or excessive wear, as the case may be, whereas if the optimum amount of oil were used excellent results might be obtained. The lubricant should be regarded as an integral part of a machine, and not as an auxiliary, for upon it the final success of the machine depends. The engineer who pays careful attention to matters relating to lubrication is well rewarded; he curtails fuel bills, establishment charges, repair bills, and mental anxiety.

So often does the question of price influence a buyer that a few remarks upon this subject might not be out of place. The value of a lubricant is not directly proportional to its market price. A low-priced oil may be exceedingly wasteful in consumption, and create endless trouble; in fact, it is almost an axiom that a genuine high-priced oil is more economical than a low-priced oil—even if it were a gift. There are cases, of course, when a low-priced oil can be used, but not necessarily with any advantage beyond initial cost. The merits of a lubricant are soon revealed to those engineers who keep careful records, for they can readily ascertain the difference in the cost of power, attendance charges, etc., when trying a new lubricant. The merits of a lubricant are much more apparent when the lubricant is used on a large scale, when friction losses are manifested. Suppose 1 h.-p. per annum costs £8, and in a works where 100 h.-p. is used, then the cost would be £800 per annum. If now by the substitution of another lubricant at an increased price of 2d. per gallon and only 1 h.-p. per annum is saved, it is perfectly obvious that the change would be more than justified. Again, suppose that the high-pressure valves of an air compressor can have their lives doubled by substituting a lubricant which generates the minimum of free acid, or a turbine oil giving less solid deposit, or a crank chamber oil giving less emulsion, it is evident that an extra few pence per gallon is well worth spending. Numerous other examples might be cited to emphasize this point. In brief, the question resolves itself into whether the difference in price between any two lubricants is greater than the *total* saving effected. All lubricants of the same price are not necessarily of the same value.

There are no simple rules to guide a would-be purchaser of lubricants. The subject of lubrication is difficult and complex. Almost every type of machine demands special consideration in the selection of a lubricant for it. There are, however, some very definite facts to be considered when dealing with certain types of machines. Perhaps the most important, and the one which is almost invariably omitted from specifications because it is taken for granted, is that the oil shall be tolerably free from sulphur compounds.

Various specifications have from time to time been formulated by divers persons for various lubricants; some merely specifying the specific gravity, viscosity, others include that the oil shall be a pure hydrocarbon or a compound oil; others that the oil shall have a certain demulsification value, or sludge value. The surface tension of the oil has been suggested, but it is extremely doubtful, for reasons given elsewhere, whether this will ever be universally adopted. It is a curious fact that the colour of the oil is very rarely stated in spite of its importance.

Specifications are exceedingly difficult to prepare without a very intimate knowledge of the subject. A specification is compiled primarily to ensure the supply of a specific commodity; therefore if the specification is incomplete, as so many specifications are, the would-be purchaser may buy in good faith from a vendor who sells in good faith, and yet the commodity may fail in its purpose.

Unfortunately there are very few chemists outside the oil industry who have sufficient knowledge of lubricants to write or interpret a specification for lubricating oils, and, further, the opportunity for acquiring the necessary special knowledge is practically nil at the present time. Hence the public are in that unenviable position of being practically at the mercy of the oil industry. This being so, any specification which might be adopted should be accompanied by a sample of the oil to which the specification applies, together with details of the purpose for which the oil is intended. Then the possibilities of misinterpretation are diminished.

Specific gravity is of limited value in selecting a lubricant. Oils of similar gravity might be good or bad for any particular purpose. A high gravity oil might point to a poor Pennsylvanian oil, or a high-class Texas oil, or to a good Pennsylvanian oil compounded with a high gravity fatty oil. Likewise a low gravity oil might indicate several possibilities. It is useful, however, to check quantities if the oil be purchased either by weight or by volume.

It is a common practice in the trade to sell lubricating oil at the rate of 9 lb. to the gallon. Hence with high gravity oils less than a measured gallon will be obtained, and with low gravity oils more than a measured gallon.

Viscosity is an essential feature of any specification. If possible the viscosity should be stated at the temperature at which the oil is to work. As this is very frequently difficult to obtain, it is customary to state the viscosity at two or more temperatures. In the case of oils working at *circa* atmospheric temperature it is only necessary to state the viscosity at 60° F. or 70° F., but when the oil is used in an internal combustion engine, or on a heated surface, the viscosity at 140° F. or 200° F. should be given, or in the case of a steam cylinder oil at 200° F. and 250° F.

Occasionally the viscosity is specified in terms of some oil or substance for which no standard viscosity is universally recognised. Such practice should be discouraged, as it only leads to misunderstandings.

The temperature coefficient of viscosity, or the decrease in viscosity per unit of temperature rise, is of some considerable importance in selecting a lubricant which may have to work throughout a long range of temperature. A viscous oil at the lowest temperature might impede the working of the machine, and be too thin at the highest temperature, and therefore permit undue friction. In such a case it is necessary to have a lubricant which will maintain its viscosity at elevated temperatures.

Flash point is almost invariably stated in specifications, and given in reports; consequently it has become to be regarded as a figure of some importance, but what significance it possesses one rarely pauses to consider. Primarily the flash point determination was devised to gauge the liability of an oil to fire when it, or its vapour, came into contact with a flame, in order to make suitable provision against fire risks. Fire insurance companies are naturally interested in the flash point of the oils which are stocked by their clients, and in order to meet the demands of the fire insurance companies oil users are interested in the flash point of the oils. When such conditions abound it is easy to understand how the demand for flash point has grown. From the insurance companies' point of view one would have thought that the fire point would have been of greater interest, except in such places in which the oil stored is enclosed. Then the fire risk is dependent upon the amount of inflammable vapour which an oil will emit at a certain temperature. As a closed flash point determination will detect such minute quantities of easily inflammable bodies the determination is apt to create unnecessary alarm. In the author's opinion, the flash point figure should be supplemented by evaporation loss at a given temperature; or perhaps it may be possible to specify a minimum difference between the closed flash point and the open flash point, and the open flash point and fire point.

Some criterion may be obtained from the flash point of the constitution of a blended oil, for generally the Californian and Texas oils have a lower flash point than have the Pennsylvanian oils of similar viscosity. Further, it may be of value in checking the assertion that an oil is steam refined, or as a supplementary means of checking deliveries.

It does not indicate the liability of an oil to fire spontaneously when in use on a hot bearing. Such an indication would be obtained from the spontaneous ignition temperature.

The value of a flash point determination must therefore depend upon the special circumstances of the case in question, and not upon any defined rule.

Loss on evaporation is essentially of economic interest, although it may be of hygienic importance when the oil is used in large quantities in a confined space where workers are employed, e.g. in factories where there is much shafting, etc., and fire and explosion risks.

Cold test must figure in reports much more freely in the future than it has done in the past. The advent of high flying in low temperatures creates a new demand for low cold test oils, also the extension of motor transport in the frigid zones. The growth of cold storage and refrigerating machines has increased the demand for low cold test oils. Electrical transformers and switches must be submerged in an oil which will withstand certain low temperatures, in order that they may work satisfactorily in the winter.

The demulsification value of an oil may be high or low, as occasion demands. For forced feed systems on steam turbines and crank chambers it is essential that an oil of high demulsification value should be used. In those crank chambers in which the oil is floated upon water and the splash system of lubrication is in vogue an oil which will give a certain amount of emulsion is necessary. Except in these special cases the demulsification value is of little importance.

The acidity should be as low as possible, but what the maximum limit should be is controversial. It appears as if various standards have become recognised by virtue of the grades of oil actually on the market: e.g. castor oil can readily be obtained with a free fatty acid value of less than 1%; lard oil of medium quality, suitable for lubrication, may have an acidity of 4% to 8%; mineral oils an acidity of less than 0·1%; hence these values are frequently quoted in specification for no other reason than that mentioned above. The mere statement of acidity, without due reference to the nature of the acid, is of doubtful value if the acidity be considered from its corrosive properties. If this be so, then acidity determinations will have to be superseded by some more exact means of measuring the corrosive action of the oil, because the corrosive action of all acids is not equal.

The liability of an oil to carbonise when in use is perhaps one of the most difficult factors to gauge in a laboratory; further, this propensity of any oil must be judged upon the nature of the machine in which it is to be employed, and the conditions to which the oil is subjected. Engines which work at high temperatures and pressures must necessarily require a lubricant with a low carbonisation value, whereas an engine working at a lower temperature and pressure can be lubricated with an oil of higher carbonisation value. The carbonisation value of any lubricant for any specific purpose can only be gauged upon a vast amount of research and practical experience. Owing to the great value of such information to the manufacturers of lubricants great care is invariably maintained to prevent the leakage of their standards to the outside world.

The formation of free acids whilst the oil is in use is of serious account in air compressors, such as are attached to Diesel engines, owing to their corrosive action upon the valves and pipes. It is only in special cases that acid formation need be considered. In those cases where it must be considered only those oils which give rise to the minimum of acid should be used.

CHAPTER X

OILS EMPLOYED

Oils Employed.—In this chapter no pretence is made to describe more than a few typical examples of engines and parts, and the lubricants employed.

Spindles are chiefly used in textile factories for carrying the bobbins upon which the yarn is wound. The speed of these spindles is frequently very high, ranging from 8000 to 12,000 r.p.m. Since it is reputed that a spindle making 7000 r.p.m. uses 0·0075 h.-p., and one making 11,000 r.p.m. uses 0·01625 h.-p., and since the number of spindles in a factory may be very great, very careful attention must be paid to their lubrication. A light mineral oil which will flow readily with the spindle ; one which will maintain a perfect film, and one which has a viscosity of about 80 seconds (Redwood) at 60° F. is generally demanded. The oil must have a minimum evaporation loss, and a maximum flash point consistent with this viscosity.

Shafting is usually classified as light, medium, and heavy ; consequently only three types of oils are thought to be necessary. Such a classification is extravagant, especially where there is much shafting. It is not uncommon to find in large mills that 25% of the total engine power is absorbed in overcoming the shafting friction, and hence the lubrication of shafting is a more important item than is frequently supposed. Pure mineral oils of the following viscosities are used.

Type of Shafting	Viscosity at 60° F.
Light . .	450 Redwood seconds
Medium . .	900 ,, ,,
Heavy . .	1800 ,, ,,

The oil should show no tendency to gum, nor thicken when in use, nor to dry, even if the bearings are running warm.

A thinner oil can be used on shafting running at higher speeds than those mentioned above. In textile mills, where the average speed may be between 300 and 400 r.p.m., a thinner oil would be used than a similar shafting in a machine shop running at about 150 r.p.m.

Bearings are so varied in character that no general classification can be made. They may be designed to carry light loads or heavy loads; high speeds or low speeds; a steady motion or a thrust; to be run at high temperatures or low temperatures.

Ball- and roller-bearings are now largely used on certain classes of machinery to reduce friction, and this they do in large measure; but they do not appear to have been adopted when the pressure is great and the speed high to any appreciable extent. It was, and is still, believed by some engineers that these types of bearings are to be run free of any lubricant, but such a belief must be discounted when one recognises the fact that dry roller- or ball-bearings, however accurately they may be made, must give rise to solid friction as the balls or rollers rotate against each other or against the races. Theoretically a light oil should be used of just sufficient viscosity to overcome that slight friction produced; but in practice a soft mineral grease is favoured owing to the infrequent applications which are necessary by its use, and its ability to exclude moisture and grit, and white compound grease may be used provided it is free from substances which will corrode the balls or rollers. A fatty oil, or a heavily compounded oil, should not be used owing to its liability to become acid and therefore corrosive. Graphite and graphite greases are not recommended.

Steam turbines are designed to work at high speeds, 1500 r.p.m. and upwards, and so to ensure a liberal supply of oil to flood the bearings the oil is fed from a reservoir by a pump at about 15 lb. pressure. The oil when it leaves the bearings is carried back through pipes to the oil reservoir via an oil cooler. Some turbines are fitted with water-cooled bearings, in which case the oil does not rise much above 120° F., but in those turbines which are not fitted with water-cooled bearings the temperature rises to about 140° F., and in exceptional cases to 160° F.

The lubricant should have a viscosity of 420 to 960 Redwood seconds at 60° F., and 70 to 95 Redwood seconds at 140° F., depending upon the make and condition of the turbine; it should have a demulsification value of not less than 90%, although one of 95% is preferred. The loss on heating for eight hours at 100° C. should not exceed 0·5%, and the sludge value should not exceed 0·7%. The oil should not develop acidity unduly. A good turbine oil should not have an acidity of greater than 0·01%, expressed as sulphuric acid, and must be free from mineral acids and alkalies.

Locomotive bearings generally carry a pressure of not exceeding 500 lb. per sq. in., and the journal revolves at not more than 270 r.p.m. Locomotive engineers in this country call for an oil containing anything from 5% to 75% of rape oil, according to their needs, in the mineral oil.

As locomotive bearings are fed with oil by syphons fitted with wool trimmings, it is imperative that the oil should syphon freely and show no tendency to clog the trimmings. Some locomotives are subjected to considerable variations in temperature in their travels, consequently the oil must be of such a character to work satisfactorily under such thermal changes. The oil must be free from asphaltic substances precipitable by petroleum spirit. The viscosity for summer use should be 2500 at 60° F., and for winter use 1800 Redwood seconds, in the British Isles. These figures are not adopted by all the British railways, although they are representative of what the large railways have standardised.

Axle-boxes are fitted either with pads from which the oil is fed to the journal, or with cotton or wool waste, which is properly packed into the box and saturated with oil, or the oil may be fed through a mechanical lubricator. For axles a cheaper oil than is used on the bearings is quite good enough, but it is a mistake to use inferior oil, for by so doing hot boxes must inevitably result.

Marine engine bearings are subjected to duty for much longer periods than land engine bearings would be ordinarily subjected. Furthermore, the bearing pressures are frequently higher, running up to about 750 lb. per sq. in.; consequently more care must be taken to avoid the bearings running hot, and if they should, to have adequate means of reducing their temperature quickly. It is common practice to turn a hose-pipe on a heated bearing. The antidote is as simple as it is effective provided the oil film is not destroyed, for if it were a worse state of affairs would result. To meet this contingency marine bearing oils are usually compounded with large quantities of rape or blown rape oil, so that the oil will emulsify with the water if water should get into the bearings. It is frequently stated that marine engine oil containing blown rape separates on standing, and therefore the oil should be well mixed before using. An oil which will separate on standing should be condemned, for an oil to separate into its respective constituents shows conclusively that it has not been correctly blended. A lubricating oil must be homogeneous.

Viscosity of the oil should be between 2700 and 3600 Redwood seconds at 60° F.

Tunnel bearings are lubricated either with block grease or heavy mineral oil.

The tail-end shaft is practically inaccessible when the ship is afloat, and therefore it is highly important that no risk should be taken with the lubrication of this end of the propeller shaft. With this in mind, it is not surprising to find that those few firms who have studied stern tube lubrication should regard their special lubricant as a proprietary article.

For extra heavy bearings sometimes castor oil is used, but now as it is possible to obtain a mineral oil whose temperature coefficient of viscosity is practically equal to that of castor oil, the latter is used on account of its lower price and its freedom from acidifying and gumming propensities. The feature of castor oil is its durability.

Castor oil has a viscosity of about 6000 Redwood seconds at 60° F., 320 Redwood seconds at 140° F., and 97 seconds at 200° F.

Motor-car engines and petrol engines in general are lubricated with one oil, that is to say the oil for the bearings and cylinders is all fed from the one sump. The oil is usually fed by force feed to the various parts, and the excess flows back to the sump. In some engines the splash system is adopted. Owing to the large number of makes of engines a tabulated list of standard makes is given, with the lubricant recommended for each make.

The following list shows the most suitable grades of Wakefield "Castrol" for the makes mentioned:

Make	"Castrol" Oil Grade
A.B.C.	C
A.C.	XL
Airedale	A
Albert	A
Alldays	A
Angus Sanderson	CW
Argyll	CW
Armstrong-Siddeley	A
Armstrong-Whitworth	A
Arrol-Johnson	A
Ashton	XL
Austin	CW
Autocrat	CW
A.V.	C
Baguley	MP
Bayard	A
Bean	C
Beardmore	A
Bedford-Buick	CW
Bellanger	A
Belsize	A
Bentley	C
Berliet	MP
Bianchi	MP
Biford	MP
Bleriot Whippet	C
Brasier	MP
Briscoe	CW
Briton	C
B.S.A.	XL
Buchet	MP
Cadillac	CW
Calcott	A
Calthrope	A
Calthrope Minor	C
C.A.R.	C
Chalmers	CW
Chandler	CW
Charron	A
Chenard-Walcker	MP
Chevrolet	CW
Citroen	A
Clement-Talbot	CW
Columbia	CW
Coventry Premier	XL
Crossley	CW
Crouch	C
Cubitt	A
Cycar	C
Daimler	K
Darracq	MP
Dawson	C
Day-Leeds	CW
De Dion	GP
Deemster	A
Delage	MP
Delahaye	C
Delaunay	A
D.F.P.	MP
Dodge Bros.	CW
Douglas	XL
Duplex	C
Enfield-Allday	C
Eric Campbell	XL
Essex	CW
Farman	A
F.A.S.T.	C
F.I.A.T.	C
F.L.	A

Make	"Castrol" Oil Grade
Flanders	CW
Ford	F
Germain	CW
Gladiator	C
G.N.	C
Grahame-White (Buckboard)	C
Gregoire	MP
Guy	GC
G.W.K	C
Hampton	C
H.E.	C
H.F.G.	A
Hillman	XL
Hispano-Suiza	XL
Hortsmann	XL
Hotchkiss	A
Hudson	A
Humber	MP
Humberette (water-cooled)	A
Do. (air-cooled)	C
Hupmobile	CW
Hurtu	C
Iris	A
Isotta-Fraschini	C
Itala	A
Jowett	XL
King	CW
Kingsbury Junior	XL
La Buire	A
Lagonda	CW
Lanchester	CW
Lancia	C
Landseer	CW
La Ponette	A
Lawrence-Jackson	C
Léon Bollée	CW
Liberty	CW
Little Midland	C
L.M.	C
Lorraine-Dietrich	MP
Maibohn	A
Majola	C
Marlborough	CW
Martini	A
Mascotte	C
Mass	A
Mathis	CW
Maudsley	CW
Maxwell	CW
M.B.	C
Melton	C
Mendip	A
Mercedes	A
Mercury	A
Metallurgique	C
Meteor	XL
Meteorite	XL
Minerva	XL
Mitchell	CW
Moon	CW
Morgan	C
Morris-Cowley	XL
Morris-Oxford	XL
Mors	A
Motoblock	C
Napier	XL
Nazarro	C
Newey	C
New Orleans	C
Newton	A

Make	"Castrol" Oil Grade
Oakland	A
Oldsmobile	A
Opel	CW
Overland	CW
Paige	CW
Palladium	C
Panhard	A
Panhard-Knight	K
Peerless	A
Perry	CW
Peugot	XL
Peugot (valveless)	CW
Phœnix	A
Piccard-Pictet	A
Piercè-Arrow	CW
Pilain	C
Pullman	CW
Renault	A
Richardson	C
Riley	C
Roamer	A
Rolland-Pilain	C
Rolls-Royce	R
Rover	A
Rover (air-cooled)	C
Rustin and Hornsby	A
Sava	A
Saxon	A
S.C.A.T.	C
Schneider	A
Scout	A
Scripp's-Booth	F
Sheffield Simplex	A
Siddeley-Deasy	A
Sigma	C
Singer	A
Sizaire-Berwick	XL
Sizaire-Naudin	CW
S.P.A.	A
Stafford	A
Standard	A
Star	A
Straker-Squire	A
Studebaker	CW
Sunbeam	A
Swift	CW
Talbot Darracq	XL
Tamplin	C
Taunton	A
T.B.	C
Templar	CW
Thanet	A
Thor	A
Thornycroft	CW
Unic	A
Varley-Woods	C
Vauxhall	CW
Victor	C
Vinot	GP
Voisin	A
Vulcan	A
Waverley	A
Wilton	A
Wolseley	A
Zedal	A
Zephyr	C

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There is no general rule to help one to decide whether a pure mineral oil or a compound oil shall be used. Some types of engines will run perfectly with a mineral oil, whilst others will only give satisfaction with a compound oil. The differentiation between these engines is a matter for a practical trial. Similarly difficulties arise when deciding upon the viscosity of the oil to be used. In some measure assistance is gained by the fact that a two-stroke engine requires a more viscous oil than a four-stroke engine of the same size; that the shorter the stroke in comparison with the diameter of the cylinder the greater the viscosity of the oil, and that air-cooled engines require a higher viscosity oil than a water-cooled engine.

The gears and back axles may be designed for grease or oil lubrication; the oil system appears to be gaining favour now that it is recognised that oil offers less resistance to the teeth than grease. The difficulty in the use of oil is to prevent it from leaking from the gear-box or back axle through the bearings and creeping on to the brake drums.

Agricultural tractors might be classed as petrol engines were it not for the fact that for cheapness they run on paraffin instead of petrol. On those engines which use paraffin for fuel a viscous oil is desirable, partly to compensate for the reduction of viscosity caused by the mixing of the unburnt paraffin with the oil.

Aero engines of the rotary type are almost invariably lubricated with castor oil or Castrol "R," a lubricant made by blending castor oil with mineral oil. The novelty about this oil is that the mineral oil is homogeneously dispersed in the castor oil, whereas mineral oils are believed to be practically insoluble in untreated castor oil. The makers of this oil claim that it is superior to castor oil in its lubricating qualities, that it has a lower cold test, and is a cleaner oil in the engine. Castrol "R" is also used on stationary petrol engines when great efficiency is demanded, such as for aeroplanes, airships, racing motor-cars, etc.

Gas and oil engines, also, are generally supplied with a double-purpose oil. The considerations which govern the selection of the type of lubricant employed are closely allied to those prevailing with petrol engines. The viscosity is generally agreed upon to be

Up to 50 h.-p. per cylinder, 720 Redwood secs. at 60° F,
Above 50 h.-p. ,, 1800 ,, ,, ,,

Diesel engines are oil engines of a different class and warrant special consideration. Air compressors form an integral part of a Diesel set, and therefore must be treated with the main prime mover. The compressor is driven off the crank-shaft to supply air at a sufficiently high pressure to force the fuel oil into the cylinder of the engine. Although the compressor is the minor portion of the set it is the part which frequently demands most attention, mainly because its duties are most arduous, it having to supply air at 700 lb. to 1000 lb. per sq. in. Air being compressed to this pressure needs very efficient cooling to prevent it from becoming a very active and dangerous article. Even when it is cooled to reasonable working temperatures it is not without action upon the lubricating oil, and through this alone fatal accidents have occurred; consequently it is imperative to use an oil which shall be the least affected, not merely as a preventive from accidents, but for economy in working. Any oil but the very best will carbonise in the cylinders and produce acid which corrodes the valves and pipes, the evils of which are best known to engineers in charge of such sets.

The lubrication of the engine is frequently separate from that of the compressor, although the same lubricant may be used on both. On the engine the oil is in constant circulation, whereas on the compressor only new oil is supplied.

A mineral oil only should be used of the very highest quality, and should have a viscosity of 120 Redwood seconds at 140° F., and 52 seconds at 200° F., and for engines of 200 h.-p. and above per line 162 seconds at 140° F., and 65 seconds at 200° F.

A paper dealing with this subject was read by the author before the Diesel Engine Users' Association at the January and February meetings, 1917. To illustrate the advantages of correct lubrication a report from P. H. Smith, the authority on Diesel engines, is of interest.

He states:

"Between January and the middle of May we ran on a very well-known oil, and results were as follows:

Hours run	1720
Units generated . . .	166308
Load factor, per cent . . .	64
Oil per 100 running hours .	16·6 gallons
Oil per 1000 units . . .	1·74 ,,

"Then the crank-case was cleaned out and your Deusol employed.

Hours run	3001½
Units generated	334810
Load factor, per cent	74
Oil per 100 running hours	5·3 gallons
Oil per 1000 units	0·48 gallons."

Dynamos and electric motors are so closely allied that for purposes of lubrication they may be classed together. Owing to the simplicity of their bearings, and high speed, their lubrication is not one of any difficulty, although occasionally strange, and unsuitable, lubricants are employed. Only a mineral oil having a viscosity of 480 to 1000 Redwood seconds at 60° F., according to the size and speed of the motor, should be used.

Transformer oil is used for keeping cool the windings of electrical transformers. The properties of such oil are at the present moment being investigated by the Electrical Research Committee, of which the author is a member, and until the findings are published no standard specification can be given. Suffice it then to say that the oil shall have a high dielectric strength to ensure perfect insulation of the windings, low evaporation loss for economy in working, a flash point of not less than 160° C., free from acidity, and a minimum tendency to form solid deposits when in use.

The characteristics of the oil used in electric switches are almost identical with those of transformer oil.

Steam cylinder lubrication is perhaps one of the most difficult branches of lubrication, and it must be acknowledged that there is a great deal of research still to be done before the subject can be claimed to be thoroughly understood. A great deal of work has been done by the author and others to explain the formation of carbon deposits, and the production of lubricants to meet the conditions encountered. Briefly, it may be stated that a good mineral oil does not carbonise when subjected to *pure* steam even at a pressure of 200 lb. per sq. in. and at a temperature of 1000° F., but when air is introduced to the hot cylinder carbonisation can take place, or when coal ash is conveyed into the cylinder, or particles of oxide of iron, or when priming occurs. The reaction which takes place under these conditions is being investigated in the hope of being able to eliminate completely those substances in the oil which contribute to the formation of the carbon deposits. By correct application of the oil through an anti-carboniser, or other device, and by special treatment of the oil considerable advance has been made in the satisfactory lubrication of steam cylinders, and the steam valves, during the past few years.

Pure mineral oils of high viscosity are favoured by some engineers acting on the belief that compound oils are hydrolysed by the steam, and the resulting free fatty acids corrode the metal. A large number of experiments have been made by the author to test this belief, but as far as steel and iron are concerned he is unable to find, under working conditions, sufficient justification for the belief. When the steam is condensed and returned to the boiler, as in marine practice, a pure mineral oil should be used to avoid the risk of the conveyance of troublesome free fatty acids into the boiler, which might occur if a compound oil were used. Furthermore, owing to the continuous working of a marine engine, and the same thing applies to other continuous running steam engines having cylinders, a mineral oil can be used owing to the absence of condensation of steam in the cylinder, with the attendant risk of reducing the efficiency of the oil film. In those engines which are intermittently run, and where condensation of steam is possible in the cylinders, as in locomotives or winding engines, a compound oil is always preferable, to ensure a more stable film when water is present.

The best cylinder oils contain from 2% to 10% of fatty oil, and have a viscosity of 130 to 230 Redwood seconds at 200° F., depending upon the conditions in the cylinder. It is not customary to take the viscosity of cylinder oils at temperatures above 250° F. To take it at higher temperatures would be very difficult in a Redwood viscometer, and for practical purposes unnecessary, for we know that an oil with a viscosity of 230 Redwood seconds at 200° F. is sufficiently viscous for working temperatures even above 700° F. More viscous oils can be obtained, but apparently they are unnecessary under present conditions. The actual pressure on the cylinder wall when the piston is working is probably very small; the author is of the opinion that the pressure is thrust upon the cross-head, and the greater the steam pressure the less the pressure, as it will tend to float the piston. It is for this reason that it is possible to use such a thin oil at the working temperatures of the cylinder. Since all ordinary cylinder oils are black it is advisable to estimate the asphaltic substances present, as these compounds would give an oil a fictitious high viscosity.

Almost invariably it is stated that the flash point of the oil should be above the temperature of the steam. The reason for this the author cannnot understand, because when the oil passes into the steam there is no chance of the oil flashing. True an oil with a high flash point is almost invariably a viscous oil with a low evaporation loss, but on the other hand a low flash oil does not necessarily indicate a low viscosity nor high evaporation loss, because a minute quantity of a low flashing oil will diminish the flash point considerably. Still, to safeguard oneself it might be advisable to use an oil whose flash point is 500° F., or above, as a check upon the refiner.

It has been suggested that the value of a steam cylinder oil is proportional to the non-volatile portion of the oil in steam at the temperature at which the oil is to work, on the supposition that only the non-volatile oil remains to provide the oil film, the remainder being carried away in the steam. If the oil were fed directly to the cylinder wall through a quill it is conceivable that this might be substantiated in fact, but the weakness of the theory is that the non-volatile portion is the very fraction of the oil which will give rise to carbonisation. Further, such a theory cannot be reconciled with the modern practice of complete atomisation of the oil previous to its entry into the cylinder.

Steel rolling is done by passing the metal, either hot or cold, through metal rollers under pressure. When the steel is rolled hot no lubricant is used, but when it is done cold the metal is placed in an acid bath to remove any iron oxide on the surface of the metal; then it is drawn through the rollers to reduce its thickness, or to shape it. The acid must be removed from the metal as it passes through the rollers, otherwise corrosion of the metal would subsequently take place; also the bright rollers, which are very accurately made, must be protected from the acid. To do this oil is applied to the metal and the rollers of such a nature as to absorb the acid. Rape oil has been used for many years with satisfactory results, but owing to its high price a satisfactory cheaper oil has been sought. Several mineral oils have been tried and condemned, also combinations of rape oil and mineral oil; any such combination containing less than 75% of rape oil is reputed to be unsatisfactory. The author has evolved an oil which, whilst very much less expensive than rape oil, completely removes the acid from the metal and protects the rollers, and gives just sufficient lubrication to enable the metal to pass through the rollers evenly without overheating or slipping, and so obviate the possibility of uneven rolling.

Brass rolling is conducted in a similar manner to steel rolling. In this class of work, also, rape oil is being substituted by a cheaper oil.

The presses contain two or more steel rollers which are provided with journals, sometimes the same diameter as the roller. The journals run in bearings, the pressure on which is governed by the rolling requirements ; generally it is very great. High melting-point grease is used in some mills, whereas beef suet is used in others, and the bearings are kept cool by a stream of cold water. Modern practice calls for a good viscous mineral oil applied by a mechanical lubricator. The efficiency of the method, apart from the capabilities of the oil, is the power of the lubricator to supply the oil to the bearing under such high pressures.

Cutting oils, such as are used on lathes, drills, screw-cutting tools, etc., have been modified during the past few years. The idea that the oil acted as a lubricant between the cutting edge of the tool and the metal being cut is now regarded with doubt. The pressure at the knife-edge, it is reputed, may be as high as 100,000 lb. per sq. in. ! During the cutting a considerable amount of heat is generated which must be dispersed to prevent damage to the tool, and incidental loss of overall efficiency by poor cutting, increased motive power, diminished output through regrinding and refitting. The oil must cool the tool and lubricate the face of the tool over which the chip has to pass.

For cutting soft metal water could be used were it not for the fact that it would rust the metal, so an emulsifiable oil is added to the water. Various soluble oils are on the market which can be mixed directly with water in the proportion of one part of oil to thirty parts of water, giving a milky emulsion. Semi-solid cutting compounds are also used, but these require more labour in mixing with water than do the soluble oils.

A soluble oil or cutting compound should give a stable emulsion when mixed with water in the proportion recommended for use by the suppliers, and should act as a rust preventive. Further, it should be antiseptic, and capable of rendering a wound aseptic if a worker should receive an injury whilst working.

Work which demands a fine finish is always cut under a flow of oil. In the past lard oil was almost exclusively used, but recently it has been found that lard oil substitutes give satisfactory results at an infinitely lower cost, and are free from the objectionable propensity towards rancidity. Some difficulty has been experienced in finding a suitable oil for use in cutting very hard metals. This difficulty has been investigated and solved by the author.

As in the case of soluble oils cutting oils should be antiseptic.

The oils used for metal quenching have either been whale, cod, or sperm, and until lately their supersession has never been attempted seriously. Their particular characteristics as quenching mediums can be copied in mineral oils; such characteristics as even quenching without creating distortion, freedom from undue fire risks, absence of thickening of oil when in use, and non-production of deposits liable to clog the oil cooler. Mineral quenching oils are free from the objectionable property of the fish oils, of producing objectionable odours during quenching.

Fire risks are extremely important considerations in any works, and must therefore be carefully considered in adopting an oil for quenching, especially where large pieces of metal are to be quenched. The flash point of a quenching oil is of very little value in gauging the fire risks; what one has to consider is the spontaneous ignition temperature, i.e. that temperature at which the oil will burst into flame without the application of a spark or other local high temperature. The hot metal takes time to be immersed in the oil, the period being in some measure dependent upon the dimensions of the metal and the facilities for handling it; consequently any oil vapour which is produced is exposed to the heat of the metal for that period which is occupied in lowering the metal into the oil. If the period be short, and the surface area of the metal be small, there is little risk of fire, but if the surface area be large, and the period long, the thermal transference of the oil must be sufficient to convey the heat sufficiently rapidly from the hot zone, and thereby reduce the vaporisation of the oil, and so reduce the fire risk, also it must have a high spontaneous ignition temperature to ensure that the vapours will not ignite when in contact with the hot metal above the oil. However suitable an oil may be, if it be worked until its temperature exceeds a temperature of 180° F. great care must be exercised. When heavy loading of the oil is practised it is customary and advisable to use an oil cooler.

The type of oil used varies with the class of quenching done, whether it be big guns, springs, or needles; each class has to be considered individually.

Tempering oil must be of high open flash point, low evaporation loss, freedom from tendency to deposit solid products when in use, and, as far as possible, odourless.

APPENDIX

" Treatment of Corks used in Soxhlet and other Extraction Apparatus."—T. J. Ward (*Analyst*, 1917, 42, 326–327). Gelatin is soaked in cold water for five hours, the unabsorbed water is decanted, the gelatin is heated until melted, and mixed with ¼ volume of glycerol and 2 volumes of water. The corks, previously bored, are immersed in this solution and heated in the same for two hours on a water-bath ; they are then removed, wiped, and dried in a warm place. Corks thus treated are impervious to the vapours of ether, light petroleum, benzene, and carbon disulphide, and do not yield any extractives to these solvents.

INDEX

ABSOLUTE units, 30, 36
Accuracy, 28
Acetylation, 65
Acetylene, 78
Acid, acetic, 96
— butyric, 96
— formic, 96
— free, fatty, 9, 59
— — — content, 66
— hypochlorous, 90
— isopalmitic, 96
— lignoceric, 96
— metaphosphoric, 87
— oleic, 98
— palmitic, 98
— picric, 91
— stearic, 98
Acidity, 58, 107
Adam, 77
Adsorption, 6
Aeronautical inspection, 44
Agrigentum, 2
Air compressor, 103
— regulator, 47
Alcoholic potash, 61
Alcohols, secondary, 6
— tertiary, 6
Alfreton, 3, 9
Alkali value, 60
Allen, 60
Aluminium chloride, 91, 94
America, North, 10
— South, 9, 10
Amiano, 2
Amylene, 84
Anæsthetics, 6
Animal charcoal, 6
Anti-carboniser, 118
Antiseptic, 120
Archbutt, 43
Ardericca, 2
Aromatic hydrocarbons, 7
Asphalt, 2, 82, 83
— maximum amount, 83
— production of, 93
Assyria, 1
Axle-boxes, 110
— back, 115

BAGDAD, 2
Baker, 3, 4, 94
Barium peroxide, 94
Bartoli, 53
Bauxite, 6
Bearings, 109
— ball, 109
— extra heavy, 111
— locomotive, 109
— marine engine, 110
— roller, 109
— tunnel, 111
Bergman, 96
Betton's British oil, 3
Blitz, 71
Block grease, 111
Bobbins, 108
Bomb, 74
Bramah, 9
Brass rolling, 120
British Isles, 14
Bromine value, 71
Brooks, 6, 96
Burma, 4, 9
Burner, 3
Burning oils, 6

CALCIUM chloride, 17
California, 5
Calories, 51
Calorimeter, 49
— ice, 50
Canada, 4
Caoutchouc, 87
Carbon, 82
— dioxide, 41
— residue, 84
Carbonisation, 95, 117
Carboxyl, 98
Carriage axles, 83
Castor beans, 9
— oil, 16, 21, 44
Castrol, 112

Catalyst, 9, 82, 95
Caucasus, 2
Centrifuge, 78
Cetyl alcohol, 98
Chambauvet, 9
Chemical tests, 58
Chill point, 44
Chlorine, 90
Classification, 21
Coke value, 86
Cold test, 41, 106
Colloids, 49
Colour, 92
Commercial purposes, 28
Compound oils, 62, 63, 65
Continent, 9, 36
Conversion tables, 36
Copra, 8
Corrosion, 48
Corrosive property, 107
Cotton seed, 10
Crank chamber, 48, 103
Creosote, 16
Cross-head, 118
Cutting compounds, 120
— oils, 120
Cyclohexane, 84

DAVIES, 77
Demulsification value, 48, 104, [106
Derbyshire, 3
Devaux, 97
Dewar flask, 32
Dielectric strength, 77
Diesel engine, 107
Digby, 88
Diphenylethylene, 70
Distillation, 5, 56
Drake, Colonel, 3
Drills, 120
Dubbs, 95
Duckham, 88
Dudley, 42
Dynamo, 117

EAGLE, 2
East Indies, 9
Edeleanu, 6
Egloff, 7
Egypt, 9, 10
Eisenstein, 81
Electric motor, 117
Electrical Research Comm., 81, 88
Electrical resistance, 53
— stress, 94
E.M.F., 48
Emulsion, 48
Engines, aero, 115
— Diesel, 116
— four-stroke, 115
— gas, 115
— marine, 118
— oil, 115
— rotary, 115
— two-stroke, 115
— winding, 118
England, 4, 8, 9
Engler flash, 57
— Number, 30, 36
Eosin, 77
Esling, 73
Ether, 63
Evaporation, 45
Evesham, 8
Expression of results, 36
Extraction, 6

FALQUIRE, 9
Fatty acid content, 66
Fatty oils, 8
Ferric chloride, 94
Filtered oils, 6
Filtration, 6
Fire of Heaven, 2
— eternal, 3
— point, 18
— risks, 105, 121
— worshippers, 3
Fishing industry, 10
Flash point, closed, 11, 105
— — freaky, 16
— — open, 11, 18
Flask, Engler, 57
— Redwood, 57
Flue dust, 94
Fluid friction, 22
Foodstuff, 8
Formaldehyde, 80
"Formolit," 80
Fox, 85
Frash, 7
Freezing medium, 44
Friction losses, 103
Fuller's-earth, 6, 9

GALLENKAMP, 47
Gallitz, 95
Gans, 32
Gears, 115
Genoa, 2
Germany, 30
Gill, 34, 85
Glass chimney, 3
Glyceride, 50

Glycerol, 36, 65
— content, 65
Goldstein, 52
Graphite, 109
Gray, 84
— tester, 14
Great Britain, 2
Greeks, 2
Gripper, 62
Groschuff, 76
Gum, 84
Gumming test, 85

HANUS, 70
Hanway, 4
Hardened fat, 9
Hardy, 98
Harker, 11
Heer, 80
Herodotus, 2
Higgins, 11, 29
History of petroleum, 1
Hit, 2
Holde, 32
Holland 8, 9
Hübl, 67
Hübl and Wij compared, 71
Humphrey, 3, 6
Hydrocarbons, aromatic, 56
— methylene, 54
— unsaturated, 90
Hydrogen, 9
— sulphide, 95
Hydrogenation, 9
Hydrolysis, 59
Hydrometer, 21
Hydroxyl, 98

IGNITION temperature, 18
Illuminating, 5
India, 4, 9, 10
Inert, 64
Inflammable, 5
Insurance, 105
Internal combustion engines, 6, 56
Iodine solution, 67
Iodine and bromine values compared, 72
Iodine value, 67, 69
Italy, 2

JAPAN, 10
Java, 10
Jenney, 93
Jupiter, 2

KELVIN, Lord, 22
Kerosene, 6
Kier, 3
Koettstorfer, 60
Kohlrauch, 52

LABROUSTE, 98
Langmuir, 98
Lard oil substitute, 121
Lathes, 120
Laurin, 98
Leather, 10
Levant, 4
Lidoff, 95
Light spirit, 6
Locomotive, 109
Loss on evaporation, 45, 106
Lot's wife, 2
Lubricating, 5
Lubricants, 8
— merits of, 103
— selection of, 102
— value of, 103
Lungwitz, 87

MABERY, 52
Magnesia, 6
Marcelin, 100
Marcusson, 77, 80
Margarine, 8, 9
Marine engine, 110, 118
— — oil, 111
Marten, 42
Maxwell, 21
Mechanical tests, 102
Medicinal, 3
Mellis, 88
Mercaptans, 96
Mercury lamp, 94
Metallic oxides, 7
Method of mixtures, 49
Methylal, 80
Methylene hydrocarbons, 54
Methyl orange, 59
Mexico, 4, 5
Meyerheim, 94
Miano, 2
Michie, 47, 88, 94
Mineral oil panel, 43
Modena, 2
Moffatt, 97
Moisture, 76
Moore, 6, 7, 19
Morrell, 7
Mortar, 1
Motor-car engines, 111
Myristin, 98

NASTJUKOFF, 80
Natural gas, 3

Newfoundland, 10
New York Produce Ex., 78
Nitrogen, 5
Noah's ark, 2
Norwegian, 10

ODOROUS substances, 9
Offerman, 32
Oil, axle, 26
— blown rape, 111
— burning, 6
— castor, 8, 16, 21, 44
— — firsts, 9
— — pharm., 9
— coco-nut, 9
— cod, 10
— compound, 62, 63, 65
— cotton seed, 8
— creek, 3
— cylinder, 26
— employed, 108
— fatty, 8
— fatty, determination of, 62, 65, 66
— film, 97
— filtered, 6
— fish, 10
— linseed, 10
— lubricating, 6
— mineral, determination of, 63
— non-drying, 68
— olive, 8, 36
— palm, 9
— — kernel, 8
— rape, 8, 21
— refining, 5
— semi-drying, 68
— sperm, 21, 100
— soluble, 120
— vegetable, 8
Old Billy Smith, 3
Olefines, 6, 7, 96
Oleography, 97
Orientation, 100
Ostrejko, 93
Oxidation, 82, 93
— test, 85

PACIFIC, 9
Palmitic, 98
Palm kernels, 9
Paraffins, 81
Paraffin wax, 6, 57
Pascal, 9
Pearson, 8
Pease, 42
Pennsylvania, 3
Pennsylvania Rock Oil Co., 3
Pensky-Martens, 14
Persian, 2
Peter the Great, 4
Petrols, 6, 57
Philip, 16, 49, 78
Phosphorous pentoxide, 94
Physical tests, 11
Pipe lines, 5
Pitch, 2
Pittsburg, 3
Playfair, Lord, 3
Pliny, 9
Poisseulle, 24
Polo, 3
Polymerisation, 6, 82, 96
Porpoise, 10
Potassium permanganate, 91
— bichromate, 67
Price, 102
Prague, 2
Prometheus, 2
Propeller shaft, 111
Psalmist, 8

QUENCHING, 121

RADCLIFFE, 69, 91
Ramsbottom, 86, 87
Ravisinc rape, 9
Rayleigh, Lord, 97
Redwood flash, 57
Refrigerator, 43
Residual valence, 98
Results, expression of, 36
Rheumatism, 3
Richardson, 81
Rocks, 1
— oil, 3
Romans, 2
Rosenthal, 78
Rotary, 115
Rumble, 24
Russia, 3, 9

SALT, 1, 2
Sand, 5
Saponification equivalent, 60
— value, 59, 60
Schreiber, 64, 94
Schultz, 42
Schweitzer, 87
Screw cutting, 120
Scriptures, 2
Sea, 10
Separating funnel, 58

Shafting, 108
Shark, 10
Shrewsbury, 78
Sicily, 2
Slime, 1
Sludge, 88
— value, 104
— and colour compared, 92
— and iodine value compared, 91
Smith, 116
Soaps, 87
Sodium, 94
— acetate, 65
— carbonate, 94
— thiosulphate, 67
Sodom, 2
Sonnenfeld, 95
Southcombe, 95
Specifications, 104
Specific gravity, 20, 104
— heat, 49
Sperm whale, 10
Spindles, 108
Splash system, 107
Spontaneous ignition, 18, 106
Starch iodide, 67
Staudinger, 96
Steam cylinders, 94, 117
— superheated, 9
Steel rolling, 119
Stereoisomerism, 71
Stolzenberg, 94
Stone, 2
Storage, 43
Stracciati, 53
Sulphate, dialkyl, 6
— alkyl hydrogen, 6
Sulphides, 96
Sulphur, 5, 73, 95 104
— determination, 73
— dioxide, 6, 7, 91
Sulphuric acid, 6
Summers, 4

TAIL END SHAFT, 111
Tallow, 36
Tar, 2
Tempering, 122
Tetraphenylethylene, 70
Texas, 16
Thickners, 87
Titration, 58
Toluene, 47
Tomlinson, 97
Tower of Babel, 1
Tractors, 115
Transformer, 94, 96, 106
— oil, 87, 117
Treub, 64
Triacetin, 65
Turbine oil, 16, 48, 103

UNITED STATES, 10, 33, 36
Unsaturated compounds, 72

VAPORIMETER, 45
Viscometer, Doolittle, 23
— Engler, 26, 30
— Helmholtz, 23
— Ostwald, 23, 26
— Redwood, 23, 24
— Saybolt, 25, 33
— Universal, 34, 36
— U-tube, 23
— Von Piotrowski, 23
Viscosity, 21, 105
— absolute, 24, 29
— results, 27
— specific, 36
— temp. coeff., 105
Vitruvius, 9
Volcanoes, mud, 5

WATER, 5, 36, 94
— determination of, 77
Wax, liquid, 10, 60
— paraffin, 6
Wij, 69
Willstaetter, 95

YOUNG, 1, 3

ZALOZIECKI, 94
Zielinski, 94
Ziffer, 82
Zinc chloride, 94

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